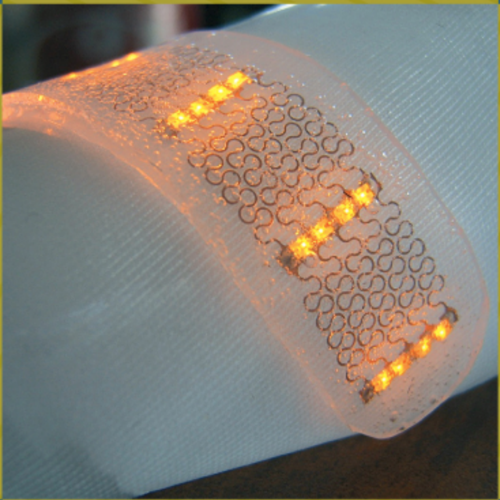
Woodhead Publishing Series in Textiles



Smart textiles for protection

Edited by R. A. Chapman

The Textile Institute

WP
WOODHEAD PUBLISHING

Smart textiles for protection

The Textile Institute and Woodhead Publishing

The Textile Institute is a unique organisation in textiles, clothing and footwear. Incorporated in England by a Royal Charter granted in 1925, the Institute has individual and corporate members in over 90 countries. The aim of the Institute is to facilitate learning, recognise achievement, reward excellence and disseminate information within the global textiles, clothing and footwear industries.

Historically, The Textile Institute has published books of interest to its members and the textile industry. To maintain this policy, the Institute has entered into partnership with Woodhead Publishing Limited to ensure that Institute members and the textile industry continue to have access to high calibre titles on textile science and technology.

Most Woodhead titles on textiles are now published in collaboration with The Textile Institute. Through this arrangement, the Institute provides an Editorial Board which advises Woodhead on appropriate titles for future publication and suggests possible editors and authors for these books. Each book published under this arrangement carries the Institute's logo.

Woodhead books published in collaboration with The Textile Institute are offered to Textile Institute members at a substantial discount. These books, together with those published by The Textile Institute that are still in print, are offered on the Woodhead website at: www.woodheadpublishing.com. Textile Institute books still in print are also available directly from the Institute's website at: www.textileinstitutebooks.com.

A list of Woodhead books on textiles science and technology, most of which have been published in collaboration with The Textile Institute, can be found towards the end of the contents pages.

Woodhead Publishing Series in Textiles: Number 133

Smart textiles for protection

Edited by

R. A. Chapman

The Textile Institute

WOODHEAD PUBLISHING

Oxford Cambridge Philadelphia New Delhi

Published by Woodhead Publishing Limited in association with The Textile Institute
Woodhead Publishing Limited, 80 High Street, Sawston, Cambridge CB22 3HJ, UK
www.woodheadpublishing.com
www.woodheadpublishingonline.com

Woodhead Publishing, 1518 Walnut Street, Suite 1100, Philadelphia, PA 19102-3406, USA

Woodhead Publishing India Private Limited, G-2, Vardaan House, 7/28 Ansari Road, Daryaganj, New Delhi – 110002, India
www.woodheadpublishingindia.com

First published 2013, Woodhead Publishing Limited

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library.

Library of Congress Control Number: 2012945572

ISBN 978-0-85709-056-0 (print)
ISBN 978-0-85709-762-0 (online)
ISSN 2042-0803 Woodhead Publishing Series in Textiles (print)
ISSN 2042-0811 Woodhead Publishing Series in Textiles (online)

The publisher's policy is to use permanent paper from mills that operate a sustainable forestry policy, and which has been manufactured from pulp which is processed using acid-free and elemental chlorine-free practices. Furthermore, the publisher ensures that the text paper and cover board used have met acceptable environmental accreditation standards.

Typeset by Toppan Best-set Premedia Limited
Printed and bound in the UK by the MPG Books Group

Contents

Contributor contact details

(* = main contact)

Editor

Mr Roger Chapman
Director
Warwick Innovation Limited
3 The Wardens
Kenilworth
Warwickshire
CV8 2UH
UK

E-mail: roger.a.chapman@btinternet.com

Chapter 1

Prof. Lieva Van Langenhove
Ghent University
Department of Textiles
Technologiepark 907
9052 Ghent
Belgium

E-mail: Lieva.vanlangenhove@ugent.be

Chapter 2

Dr Niall Finn
CSIRO Materials Science and Engineering
Geelong
Australia

E-mail: Niall.Finn@csiro.au

Chapter 3

Dr Eunkyoung Shim
The Nonwovens Institute
North Carolina State University
2401 Research Drive
Raleigh
NC 27695-8301
USA

E-mail: eshim@ncsu.edu

Chapter 4

Dr Subramanian Sundarrajan*
Department of Mechanical Engineering
National University of Singapore
2 Engineering Drive 3
Singapore 119077
Singapore

E-mail: sundarnus1@gmail.com

Dr Seeram Ramakrishna
Department of Mechanical Engineering
National University of Singapore
2 Engineering Drive 3
Singapore 119077
Singapore

and

Institute of Materials Research and Engineering
Singapore 117602
Singapore

Chapter 5

Dr Patricia I. Dolez
École de Technologie Supérieure
1100 rue Notre-Dame Ouest
Montréal
Québec H3C 1K3
Canada

E-mail: patricia.dolez@etsmtl.ca

and

CTT Group
3000 rue Boullé
Saint-Hyacinthe (Québec)
J2S 1H9
Canada

Chapter 6

Dr Ir Geert R. Langereis*, Ir Sibrecht Bouwstra and Dr Wei Chen
Eindhoven University of Technology
Department of Industrial Design
Den Dolech 2
5612 AZ Eindhoven
The Netherlands

E-mail: g.r.langereis@tue.nl

Chapter 7

Dr Veronika Kapsali
Northumbria University
School of Design London
1–15 Bradley Close
White Lion Street
London
N1 9PN
UK

E-mail: veronika.kapsali@northumbria.ac.uk

Chapter 8

Dr Huantian Cao
Department of Fashion and Apparel Studies
University of Delaware
Newark
Delaware 19716
USA

E-mail: hcao@udel.edu

Chapter 9

Prof. Jane McCann
Smart Clothes and Wearable Technology Research Centre
University of Wales, Newport
Caerleon Campus
Newport
South Wales
NP18 3QT
UK

E-mail: jane.mccann@newport.ac.uk

Chapter 10

Dr Donato Zangani
D'Appolonia S.p.A.
Via S. Nazaro, 19
16145
Genova
Italy

E-mail: donato.zangani@dappolonia.it

Chapter 11

Dr Saad Nauman
Institute of Space Technology
P.O. Box 2750
Islamabad 44000
Pakistan

E-mail: saad.nauman@ist.edu.pk

Dr Irina Cristian
Faculty of Textiles & Leather Engineering and Industrial Management
Technical University Gheorghe Asachi of Iaşi, Romania
B-dul Dimitrie Mangeron nr. 53
Iaşi, 700500
Romania

E-mail: cristian@tex.tuiasi.ro

Dr François Boussu and Prof. Vladan Koncar*
Univ. Lille North of France
ENSAIT/GEMTEX, Roubaix
2 allée Louise et Victor Champier BP 30329
59056, ROUBAIX CEDEX 1
France

E-mail: francois.boussu@ensait.fr; vladan.koncar@ensait.fr

Chapter 12

Dr Carla Hertleer*, Dr Sheilla Odhiambo and Prof. Lieva Van Langenhove
Ghent University
Department of Textiles
Technologiepark 907
9052 Ghent
Belgium

E-mail: carla.hertleer@ugent.be

Chapter 13

Mr Quoc Truong and Mr Eugene Wilusz*
Natick Soldier Research, Development and Engineering Center
US Army
USA

E-mail: eugene.wilusz.civ@mail.mil

Woodhead Publishing Series in Textiles

1 **Watson's textile design and colour Seventh edition**
Edited by Z. Grosicki

2 **Watson's advanced textile design**
Edited by Z. Grosicki

3 **Weaving Second edition**
P. R. Lord and M. H. Mohamed

4 **Handbook of textile fibres Volume 1: Natural fibres**
J. Gordon Cook

5 **Handbook of textile fibres Volume 2: Man-made fibres**
J. Gordon Cook

6 **Recycling textile and plastic waste**
Edited by A. R. Horrocks

7 **New fibers Second edition**
T. Hongu and G. O. Phillips

8 **Atlas of fibre fracture and damage to textiles Second edition**
J. W. S. Hearle, B. Lomas and W. D. Cooke

9 **Ecotextile '98**
Edited by A. R. Horrocks

10 **Physical testing of textiles**
B. P. Saville

11 **Geometric symmetry in patterns and tilings**
C. E. Horne

12 **Handbook of technical textiles**
Edited by A. R. Horrocks and S. C. Anand

13 **Textiles in automotive engineering**
W. Fung and J. M. Hardcastle

14 **Handbook of textile design**
J. Wilson

15 **High-performance fibres**
Edited by J. W. S. Hearle

16 **Knitting technology Third edition**
D. J. Spencer

17 **Medical textiles**
Edited by S. C. Anand

18 **Regenerated cellulose fibres**
Edited by C. Woodings

19 **Silk, mohair, cashmere and other luxury fibres**
Edited by R. R. Franck

20 **Smart fibres, fabrics and clothing**
Edited by X. M. Tao

21 **Yarn texturing technology**
J. W. S. Hearle, L. Hollick and D. K. Wilson

22 **Encyclopedia of textile finishing**
H-K. Rouette

23 **Coated and laminated textiles**
W. Fung

24 **Fancy yarns**
R. H. Gong and R. M. Wright

25 **Wool: Science and technology**
Edited by W. S. Simpson and G. Crawshaw

26 **Dictionary of textile finishing**
H-K. Rouette

27 **Environmental impact of textiles**
K. Slater

28 **Handbook of yarn production**
P. R. Lord

29 **Textile processing with enzymes**
Edited by A. Cavaco-Paulo and G. Gübitz

30 **The China and Hong Kong denim industry**
Y. Li, L. Yao and K. W. Yeung

31 **The World Trade Organization and international denim trading**
Y. Li, Y. Shen, L. Yao and E. Newton

32 **Chemical finishing of textiles**
W. D. Schindler and P. J. Hauser

33 **Clothing appearance and fit**
J. Fan, W. Yu and L. Hunter

34 **Handbook of fibre rope technology**
H. A. McKenna, J. W. S. Hearle and N. O'Hear

35 **Structure and mechanics of woven fabrics**
J. Hu

36 **Synthetic fibres: nylon, polyester, acrylic, polyolefin**
Edited by J. E. McIntyre

37 **Woollen and worsted woven fabric design**
E. G. Gilligan

38 **Analytical electrochemistry in textiles**
P. Westbroek, G. Priniotakis and P. Kiekens

39 **Bast and other plant fibres**
R. R. Franck

40 **Chemical testing of textiles**
Edited by Q. Fan

41 **Design and manufacture of textile composites**
Edited by A. C. Long

42 **Effect of mechanical and physical properties on fabric hand**
Edited by H. M. Behery

43 **New millennium fibers**
T. Hongu, M. Takigami and G. O. Phillips

44 **Textiles for protection**
Edited by R. A. Scott

45 **Textiles in sport**
Edited by R. Shishoo

46 **Wearable electronics and photonics**
Edited by X. M. Tao

47 **Biodegradable and sustainable fibres**
Edited by R. S. Blackburn

48 **Medical textiles and biomaterials for healthcare**
Edited by S. C. Anand, M. Miraftab, S. Rajendran and J. F. Kennedy

49 **Total colour management in textiles**
Edited by J. Xin

50 **Recycling in textiles**
Edited by Y. Wang

51 **Clothing biosensory engineering**
Y. Li and A. S. W. Wong

52 **Biomechanical engineering of textiles and clothing**
Edited by Y. Li and D. X-Q. Dai

53 **Digital printing of textiles**
Edited by H. Ujiie

54 **Intelligent textiles and clothing**
Edited by H. R. Mattila

55 **Innovation and technology of women's intimate apparel**
W. Yu, J. Fan, S. C. Harlock and S. P. Ng

56 **Thermal and moisture transport in fibrous materials**
Edited by N. Pan and P. Gibson

57 **Geosynthetics in civil engineering**
Edited by R. W. Sarsby

58 **Handbook of nonwovens**
Edited by S. Russell

59 **Cotton: Science and technology**
Edited by S. Gordon and Y-L. Hsieh

60 **Ecotextiles**
Edited by M. Miraftab and A. R. Horrocks

61 **Composite forming technologies**
Edited by A. C. Long

62 **Plasma technology for textiles**
Edited by R. Shishoo

63 **Smart textiles for medicine and healthcare**
Edited by L. Van Langenhove

64 **Sizing in clothing**
Edited by S. Ashdown

65 **Shape memory polymers and textiles**
J. Hu

66 **Environmental aspects of textile dyeing**
Edited by R. Christie

67 **Nanofibers and nanotechnology in textiles**
Edited by P. Brown and K. Stevens

68 **Physical properties of textile fibres Fourth edition**
W. E. Morton and J. W. S. Hearle

69 **Advances in apparel production**
Edited by C. Fairhurst

70 **Advances in fire retardant materials**
Edited by A. R. Horrocks and D. Price

71 **Polyesters and polyamides**
Edited by B. L. Deopura, R. Alagirusamy, M. Joshi and B. S. Gupta

72 **Advances in wool technology**
Edited by N. A. G. Johnson and I. Russell

73 **Military textiles**
Edited by E. Wilusz

74 **3D fibrous assemblies: Properties, applications and modelling of three-dimensional textile structures**
J. Hu

75 **Medical and healthcare textiles**
Edited by S. C. Anand, J. F. Kennedy, M. Miraftab and S. Rajendran

76 **Fabric testing**
Edited by J. Hu

77 **Biologically inspired textiles**
Edited by A. Abbott and M. Ellison

78 **Friction in textile materials**
Edited by B. S. Gupta

79 **Textile advances in the automotive industry**
Edited by R. Shishoo

80 **Structure and mechanics of textile fibre assemblies**
Edited by P. Schwartz

81 **Engineering textiles: Integrating the design and manufacture of textile products**
Edited by Y. E. El-Mogahzy

82 **Polyolefin fibres: Industrial and medical applications**
Edited by S. C. O. Ugbolue

83 **Smart clothes and wearable technology**
Edited by J. McCann and D. Bryson

84 **Identification of textile fibres**
Edited by M. Houck

85 **Advanced textiles for wound care**
Edited by S. Rajendran

86 **Fatigue failure of textile fibres**
Edited by M. Miraftab

87 **Advances in carpet technology**
Edited by K. Goswami

88 **Handbook of textile fibre structure Volume 1 and Volume 2**
Edited by S. J. Eichhorn, J. W. S. Hearle, M. Jaffe and T. Kikutani

89 **Advances in knitting technology**
Edited by K-F. Au

90 **Smart textile coatings and laminates**
Edited by W. C. Smith

91 **Handbook of tensile properties of textile and technical fibres**
Edited by A. R. Bunsell

92 **Interior textiles: Design and developments**
Edited by T. Rowe

93 **Textiles for cold weather apparel**
Edited by J. T. Williams

94 **Modelling and predicting textile behaviour**
Edited by X. Chen

95 **Textiles, polymers and composites for buildings**
Edited by G. Pohl

96 **Engineering apparel fabrics and garments**
J. Fan and L. Hunter

97 **Surface modification of textiles**
Edited by Q. Wei

98 **Sustainable textiles**
Edited by R. S. Blackburn

99 **Advances in yarn spinning technology**
Edited by C. A. Lawrence

100 **Handbook of medical textiles**
Edited by V. T. Bartels

101 **Technical textile yarns**
Edited by R. Alagirusamy and A. Das

102 **Applications of nonwovens in technical textiles**
Edited by R. A. Chapman

103 **Colour measurement: Principles, advances and industrial applications**
Edited by M. L. Gulrajani

104 **Fibrous and composite materials for civil engineering applications**
Edited by R. Fangueiro

105 **New product development in textiles: Innovation and production**
Edited by L.Horne

106 **Improving comfort in clothing**
Edited by G. Song

107 **Advances in textile biotechnology**
Edited by V. A. Nierstrasz and A. Cavaco-Paulo

108 **Textiles for hygiene and infection control**
Edited by B. McCarthy

109 **Nanofunctional textiles**
Edited by Y. Li

110 **Joining textiles: Principles and applications**
Edited by I. Jones and G. Stylios

111 **Soft computing in textile engineering**
Edited by A. Majumdar

112 **Textile design**
Edited by A. Briggs-Goode and K. Townsend

113 **Biotextiles as medical implants**
Edited by M. King and B. Gupta

114 **Textile thermal bioengineering**
Edited by Y. Li

115 **Woven textile structure**
B. K. Behera and P. K. Hari

116 **Handbook of textile and industrial dyeing. Volume 1: Principles, processes and types of dyes**
Edited by M. Clark

117 **Handbook of textile and industrial dyeing. Volume 2: Applications of dyes**
Edited by M. Clark

118 **Handbook of natural fibres. Volume 1: Types, properties and factors affecting breeding and cultivation**
Edited by R. Kozłowski

119 **Handbook of natural fibres. Volume 2: Processing and applications**
Edited by R. Kozłowski

120 **Functional textiles for improved performance, protection and health**
Edited by N. Pan and G. Sun

121 **Computer technology for textiles and apparel**
Edited by J. Hu

122 **Advances in military textiles and personal equipment**
Edited by E. Sparks

123 **Specialist yarn and fabric structures**
Edited by R. H. Gong

124 **Handbook of sustainable textile production**
M. I. Tobler-Rohr

125 **Woven textiles: Principles, developments and applications**
Edited by K. Gandhi

126 **Textiles and fashion: Materials design and technology**
Edited by R. Sinclair

127 **Industrial cutting of textile materials**
I. Viļumsone-Nemes

128 **Colour design: Theories and applications**
Edited by J. Best

129 **False twist textured yarns**
C. Atkinson

130 **Modelling, simulation and control of the dyeing process**
R. Shamey and X. Zhao

131 **Process control in textile manufacturing**
Edited by A. Majumdar, A. Das, R. Alagirusamy and V. K. Kothari

132 **Understanding and improving the durability of textiles**
Edited by P. A. Annis

133 **Smart textiles for protection**
Edited by R. A. Chapman

134 **Functional nanofibers and applications**
Edited by Q. Wei

135 **The global textile and clothing industry: Technological advances and future challenges**
Edited by R. Shishoo

136 **Simulation in textile technology: Theory and applications**
Edited by D. Veit

137 **Pattern cutting for clothing using CAD: How to use Lectra Modaris pattern cutting software**
M. Stott

138 **Advances in the dyeing and finishing of technical textiles**
M. L. Gulrajani

139 **Multidisciplinary know-how for smart textile development**
T. Kirstein

140 **Handbook of fire resistant textiles**
F-S. Kilinc-Balci

141 **Handbook of footwear design and manufacture**
A. Luximon

142 **Textile-led design for the active ageing population**
J. McCann and D. Bryson

143 **Optimising decision making in clothing management using artificial intelligence (AI): From production to fashion retail**
W. K. Wong, Z. X. Guo and S. Y. S. Leung

144 **Mechanisms of flat weaving technology**
V. Choogin, P. Bandara and E. Chepelyuk

145 **Innovative jacquard textile design using digital technologies**
F. Ng and J. Zhou

146 **Advances in shape memory polymers**
J. Hu

147 **Clothing manufacture management: A systematic approach to planning, scheduling and control**
J. Gersak

148 **Anthropometry, apparel sizing and design**
D. Gupta and N. Zakaria

1
Smart textiles for protection: an overview

L. VAN LANGENHOVE, Ghent University, Belgium

Abstract: Smart textiles can monitor man and his environment and react in an appropriate way. As such they are well suited for protective applications. This chapter looks at smart protective textiles from a European perspective. The Systex project is a European coordination action, targeting the enhancement of the breakthrough of smart textiles. Protection is one of the envisaged application areas. Research and technology development activities worldwide, markets, products and stakeholders are analysed. This chapter gives an overview of the potential of smart textiles for protection, ongoing developments, state-of-the-art products and future developments.

Key words: smart textiles, protection, coordination, market, policy making.

1.1 Introduction

1.1.1 Definition and importance of protection

In a period of one decade, smart or intelligent textiles have become quite well known in textile research. According to a CEN working group[1] a smart textile system consists of the following:

- actuators, possibly completed by sensors;
- an information management device that controls/manages the information within the textile system.

It is characterised by two functions:

- energy,
- external communication.

It may contain functional (e.g. electrically or optically conductive) as well as smart materials (e.g. chromic dyes, piezo-electric polymers) and electronics. Such materials are combined in a smart concept in order to achieve a specific intelligent behaviour.

Smart textile systems may have five functions:

- sensors,
- actuators,
- data processing,

- energy supply,
- communication.

A smart textile system could perform a wide range of tasks. In its simplest form it provides information about a person; the environment of the textile itself. Adequate analysis of such data may allow rapid identification of health risks. This is particularly important for protection, as it provides a chance to prevent incidents and accidents from happening. When a smart textile system detects an accident is about to happen, it could provide instant protection. After the accident has happened, it could analyse the situation and provide instant aid or call for help. Last but not least, it could support and follow up the rehabilitation process or even take over body functions that may have failed. It is quite clear that smart textile systems have a huge potential for applications in the area of protection.

On the other hand, one can question the relevance for textiles as a carrier of smart systems. Indeed, before choosing a textile as a basic tool for embedding or achieving intelligence, one must consider the added value of a textile product for the envisaged application. A first issue is that textiles are all around. We wear clothes in several layers. Our houses, working and leisure environments, in general, are decorated with carpets, textile wallpaper, curtains, upholstery on furniture, and so on. In applications for protection, advanced textiles are already available that can resist extreme conditions and/or shield from hazards such as heat and flame, chemicals, mechanical actions (cutting, bullets, etc.). So textile products offer many possibilities for integration in a discrete way, i.e. without affecting aesthetics, ease of use, or comfort.

Textiles are versatile: they can be composed of one or more polymer fibres or coatings, which can be coarse or fine (up to the nanoscale), and arranged in one, two or three dimensional structures. They are multifunctional products combining several tasks. A major advantage is their large contact area with the body without negatively affecting comfort. This allows sensoring and actuation at large and/or multiple areas of the body. Moreover, the textile product can be designed so that the active areas are always at the right place. Everyone is familiar with textiles, so no user guidelines have to be given. For industrial applications, conditions of use, including maintenance, are well defined. Textiles fit perfectly in our social context. They are widely accepted at all levels. Last but not least, manufacturing technologies are readily available, enabling large-scale production at reasonable costs.

1.1.2 History and evolution of smart textiles

Smart textiles have been around now for more than a decade. The first commercial product was developed by Philips and Levi Strauss in the

framework of the ICD+ line.[2] It consisted of a jacket with built-in mobile phone and MP3 player. A small keyboard enabled switching from one to the other device. The smart components, however, were attached to the textile, i.e. the textile was designed to integrate the wires in channels, and the devices in pockets. Before laundering, all elements had to be removed and after, they had to be put in again. In the next generation of products, the compatibility of the components were increased until they were transformed into true textile structures. Also connectivity and integration were largely improved.

The Reima suit for people riding snow scooters was the first intelligent product for protection. Built-in accelerometers detect accidents via impact. The system asks the wearer whether he or she needs help. If so, the built-in GPS system enables the rescue team to trace the victim. In the meantime, the suit provides optimal protection (e.g. shielding the victim from water, protecting hands and feet from freezing) as well as a survival kit (e.g. a flame-resistant bag to melt water by heating, a chisel to break ice). The Reima suit has not been taken to the market because of lack of a central alarm and rescue system.

Today, a range of sensors, actuators and communication tools are available, as well as flexible energy supply systems and electronics. They are compatible with textile materials in that they are flexible or stretchable, washable, and resistant to multiple deformations such as strain, bending and pressure. Some have even been made out of fibres. A workable solution is to separate the textile and non-textile component, whereby the non-textile component can be removed easily as one single-piece before washing. Press-studs are very convenient connectors in that respect, as they have both excellent electrical and mechanical contact, and are easy to apply and use.

Sensors and actuators have been developed for many applications. They are available in a textile-compatible or in true textile form. Some smart components are available at very low prices. The major cost then becomes the integration. An example is the smart bag that is discussed in Section 1.2.4. Applications range from very simple and straightforward warning systems, such as colour-change, to high-tech systems equipped with sensors, actuators, electronics and batteries. Products may address consumer markets where aesthetics overrule technical requirements. At the other end are high-risk applications, where system failure may lead to casualties.

Very important too is the data processing. Adequate use of a smart textile system requires advanced data processing. Sensors must provide data on the person and the context. Where is the person, what is he or she doing, what is the history of the person?; this is important information for assessing whether he or she is doing fine or being threatened. Moreover, each person has specific personal characteristics that may change over time.

Handling this efficiently requires advanced self-learning, context-aware data processing algorithms. More examples will be given later in this chapter, when describing actual cases of smart protective textiles.

1.1.3 Objectives of smart protective textiles

Smart protective textiles for protection can cover a wide range of applications.[3] A very low-level protective textile provides basic protection which is 'just good enough'; such textiles are often meant for wide public and private consumer markets. They can be very simple products, indicating a potential threat, such as a textile dyed with a smart dyestuff that changes colour due to its reaction with e.g. a toxic gas or UV radiation.[3] They can protect us during daily activities at work or at home. They are used by everyone as well as by specific users for dedicated tasks. The threat is related to the user and the user conditions. It can lead to small injuries up to risk of death. Some require immediate action, others allow some response time.

At the other end are connected protection systems. They collect a variety of information; advanced processing enables the assessment of complex situations. Smart textile systems can also be of such a type. They are usually meant for high-end interventions. An example is the smart fire-fighter suit PROeTEX that is described further in this chapter. Such systems contain a multitude of components. Here compatibility, interoperability, modularity, ergonomy, etc. are important factors to be considered too, apart from technological issues.

Another type of protection is against multiple risks. For some professions, the type and nature of the risk is variable and unpredictable. The military sector is a typical example. This type could require a high level of self-adaptability, so that effective protection is provided only when needed. At this moment, the appropriate actuators are still lacking.

A challenging question concerning the use of smart protective textiles is how large is the actual impact on global safety? Indeed, it has been shown that wearing protective textiles reduces the awareness and perception of danger and may lead the wearer to take more risks.[4] The overall risk is determined by multiple factors such as training, level of protection (overprotection), balance with comfort, maintenance and durability, and many others. Generally speaking, protective textiles for low-risk situations will require a high level of comfort, whereas for high-risk applications, protection and comfort have to be balanced. Here, also, smart textiles can play an important role. They can control the personal environment by heating and cooling, and by adequate moisture control and ventilation. This aspect will be addressed in Section 1.4.

Smart protective products should not cause any cognitive burden. Also for high-end applications, the product should not distract the user. It should

not require a long training period. Therefore intuitive design is very important. At this moment, very little attention has been paid to such aspects. All these factors have to be taken into account, carefully, for designing an adequate protection system. For each specific application, the set of technological solutions has to be chosen carefully. Generic solutions are rarely optimal. It may be concluded that smart textile systems can offer many benefits for applications in the area of protection. However, they have to be carefully designed, economically feasible and used in the correct way.

1.2 Smart textile functions for protection

This section describes smart textile functions in general terms. More examples will be given in subsequent sections.

1.2.1 Introduction

A smart textile can be active in many fields. It can interact with a range of parameters in different ways. For instance, it can reflect or absorb a signal. When the signal that has been absorbed can be transformed into another readable signal (e.g. colour change, current, or voltage), this can be the basis for a sensor. Conversely, an actuator can be achieved by transforming a voltage or current into the controlled release of another signal. Parameters of interaction (or signals) that have been mentioned include the following:

- temperature,
- heat flux,
- electrostatic and electromagnetic fields,
- humidity,
- chemicals in liquid or gaseous phase,
- radiation,
- movements,
- forces,
- odour,
- biological activity.

Some parameters are well known and widely-used. For fire-fighter applications, for instance, temperature is obviously very relevant. Also heart rate and respiration are generic indicators of a person's condition. Other parameters are less common or not addressed at all.

The first and most studied textile sensor is the heart rate sensor.[5–8] It was the first true textile sensor to be developed. Today, textile heart electrodes have replaced more than 50% of the traditional electrodes in sport.[9] As such, they are the first commercial success in the area of smart textiles. Such materials allow full ECG recordings. They basically consist of woven or

knitted conductive fibres. The major hurdles today are long-term stability and quality of the signals. The latter is affected by the contact with the skin and deformation of the textile. Contact with the skin varies when a person is moving, so monitoring a person at rest is easier. Sweating on the other hand contributes to a better quality of the signals. Long-term intensive use may cause the conductivity of the textile to be reduced, and ultimately the electrode may not function properly anymore. Nevertheless, today's ECG sensors have reached an acceptable level of reliability.

An example of such a sensor system is the baby pyjama developed at UGent in cooperation with the UGent University Hospital and KULeuven (Fig. 1.1).[10] It contains stainless steel fibre sensors for measuring heart signal (ECG, visible as the mice) and respiration rate (not visible on the picture). The energy supply and data transmission is achieved through an inductive link (visible as the sun) with the mattress of the bed. Consequently, the stand-alone baby pyjama does not need a battery. The concept is a perfect solution for this particular application. However, each application has its own specific requirements and boundary conditions, so use of the solution chosen for the baby pyjama may be inappropriate.

Respiration is a second type of generic sensor. Several principles have been exploited. Piezoresistive sensors based on the change in number of contacts and change in contact resistance are fairly simple: they consist of

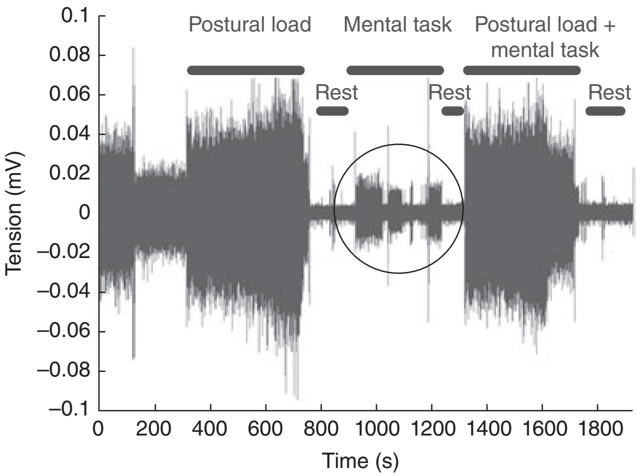
1.1 Smart baby pyjama UGent.

a spun yarn made of conductive staple fibres. Unfortunately, they are not very stable over time.[11] In addition, they measure changes in resistance and, as such, they require a power supply. Active sensors use piezoelectric materials.[12] Such materials generate an electrical charge due to deformation.

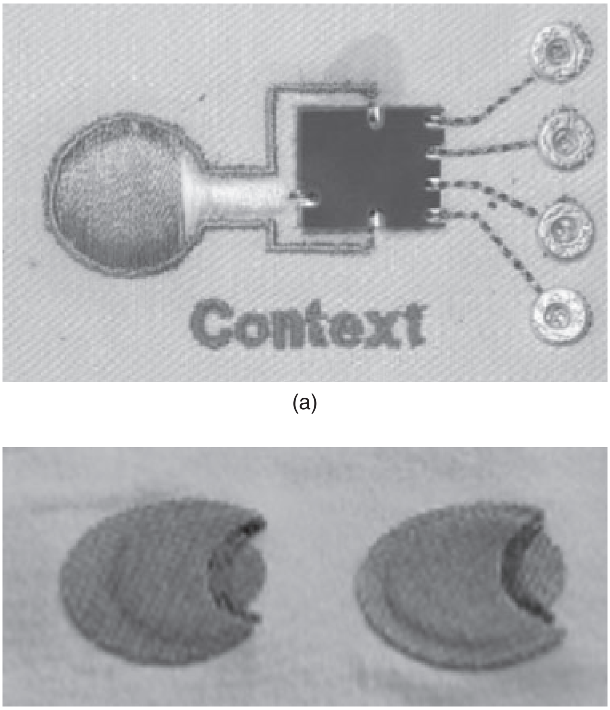
1.2.2 Protection against stress at the office

ECG sensors basically monitor the biopotential of the heart. Other muscular activity can be measured in a similar way. A particular case is the protection from the effects of continued stress in the working environment. Stress is a natural response of the body to a threatening situation. It prepares the body to fight or run away and, as such, it clearly involves a physical response. One of these responses is tensioning of the muscles. Even a mental task can cause muscle tension to increase. People working in an office carry out mental tasks and consequently they are continuously subjected to a low level of stress, especially in the trapezius muscle in the neck region. Although it is at a low level, such stress is long lasting and can cause injuries (Fig. 1.2).

Within the European project Context,[13] a contactless sensor has been developed for monitoring muscular tension of the trapezius muscle. The sensors are based on the same principles as ECG electrodes. The Context partners use embroidery and lamination technologies to produce electro myography (EMG) sensors for monitoring stress at the level of the trapezius muscle in professional situations (Figure 1.3a and b). Such systems can send out a warning to relax at regular times and, as such, become tools to prevent injuries in the long-term.



1.2 Myographical recordings as a function of activity.



(a)

(b)

1.3 (a) Embroidered and (b) laminated sensor for myography.

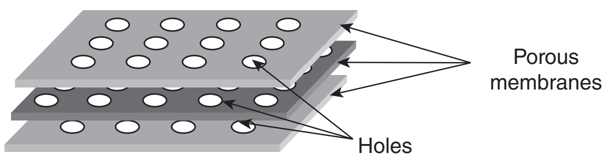
1.2.3 Military applications

Military applications have been one of the drivers for smart textiles. Soldiers are subject to a multitude of threats in a very unpredictable way. Especially in the US programme 'Soldier of the Future' that was launched in the late 1990s, the benefits of smart textiles have been studied extensively. Since then, many countries have started similar studies. NATO has sponsored two training and education initiatives on advanced textiles for civil protection and defense.[14,15] Apart from functional materials, smart textiles are considered as the backbone for the war fighter. In addition to sensor suits, there is a demand for optics, camouflage and signature management, systems for reduction of the logistic burden and enhanced mobility and survivability, reduction of heat stress, antennae and many more.[16]

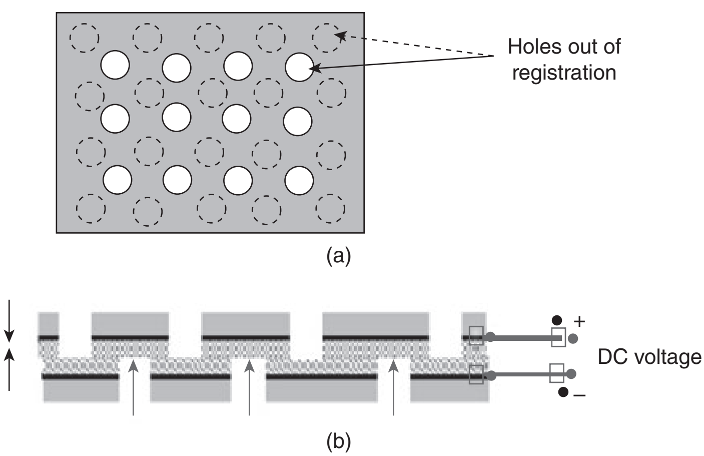
Protecting yourself often corresponds to shutting yourself down from the environment. This has a negative effect on comfort. Protection often being required only for a limited part of the time for many applications, adaptive systems would considerably improve the balance between protection and comfort. Passive adaptive systems use shape memory materials

and structures for achieving ventilation and breathability as a function of temperature. A commercial product that can be mentioned in this respect is Diaplex.[17] A first adaptive system has been developed by Natick. It consists of a multilayer structure of membranes with holes (Fig. 1.4). The holes in each layer are in different positions. In normal conditions the membranes are separated so that good permeability is guaranteed. When toxic compounds have been detected by sensors, the built-in electroactive materials are activated and this generates electrostatic attraction between the layers. As shown in Fig. 1.5a, the holes in the layers being in different positions with no overlap, the multilayer structure now becomes impermeable.

An active adaptive membrane has been developed by Martin *et al.*[18] It combines a conductive polymer with a polyurethane support, tethered with ionic groups. The tethers are the active component. In their oxidized state, they form ion pairs with the conductive polymer, causing the pores to open. In their reduced state, the free tethers close the pores (Fig. 1.5b). A small voltage suffices to switch between the open and closed state in a reversible way. Dimethylterthiophene (DMTP) is used as a conductive polymer, oxyethylenes as a tether. Oxyethylenes allow high flexibility of tether to promote intramolecular ion-pairing with the conducting polymer. The pores



1.4 Multilayer structure for active adaptive permeability – open.



1.5 Multilayer structure for active adaptive permeability – closed. (a) Top view and (b) side view.

are of nanometer size. The membrane has been applied on a polyamide substrate and tested successfully with CEES (simulant of mustard gas). The water vapour permeability in the open state is similar to that of Teflon (PTFE).

Smart textiles can also play a role in camouflage. Smart dyes can adopt the colour of the environment. X'tal Vision has developed a system consisting of projecting an image taken of the view behind a person's back, on to the front of his clothing, which renders the person invisible.[19,20] Nanocameras and textile displays will enable full textile integration of such a set up. Metamaterials can be used for redirecting light rays around an object and setting them back on path out the opposite end. So as far as one can tell, the light moves in a perfectly straight path instead of reflecting off the object as it normally would. The object has virtually become invisible.[21] Most results have been achieved on 2D structures and on wavelengths out of the visible range.

1.2.4 Protection of the citizen

Protection of the citizen is a challenge, because the number of potential threats is huge and so is the variety of situations. Solutions must be very accessible, simple, universal and straightforward, not to mention low cost. The citizen may have to be protected against chemical, physical, biological and mechanical hazards. Warning enables people to escape from the threat or to use protection in time. The smart warning system can be embedded in the environment – for instance in wall coverings or carpets, or in clothes. An example is children's clothes that change colour as a function of UV intensity: they warn parents to take their child out of the sun or to put on high SPF sun cream.

The smart bag developed by UGent students detects the presence of high intensity electromagnetic radiation emitted by mobile phones. It is a full stand-alone component including sensor, data processing and a battery. It provides a current that switches on the LEDs that have been embedded in the heart of the flowers via conductive textile yarns (Fig. 1.6). The electronics are commercially available, as well as the LEDs, so integration is the only challenge. The components being very cheap, integration is the main cost. Motor cyclists and horse riders are particularly sensitive to injuries when they fall. Mugen Denko pioneered the development of airbag jackets in 1995 and conducted many tests, although the idea was initially patented in Hungary in 1976.[22] They are now commercialised by Hit-Air.

1.2.5 Lighting applications: optical actuators

Lighting or illuminating textiles have a lot to offer in protection. High visibility is definitely an important application field for personal

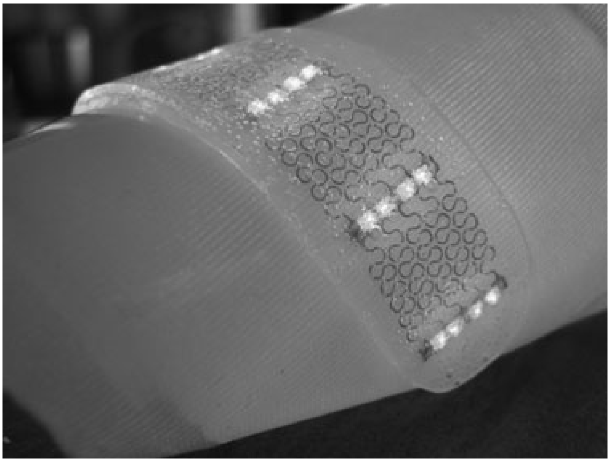
1.6 Smart bag for detection of EM radiation.

protective equipment (PPE). Also visual communication is relevant in some areas.

Illumination can be achieved by a range of concepts. The first concept was developed by France Telecom in cooperation with ENSAIT. They use optical fibres that emit light in designated areas.[23] This effect can be achieved easily by damaging the cladding layer of the fibres as this causes the light to be emitted. The team has developed a shirt with embedded optical fibres in an 8*8 matrix. Each group of optical fibres in each 'pixel' is lit by a small LED. The shirt is meant as a visual communication tool when the noise of the environment does not allow communication by sound. The system is quite bulky and energy consuming.

A second concept is attached or built-in LEDs. The Philips programme Lumalive[24] and the flexstretch concept (Fig. 1.7) are the most advanced systems in this respect. They are stretchable and fully washable.

Although meant for leisure, the Twirkle shirt made by CuteCircuit can also be mentioned; it is the first commercial illuminating product that can be purchased via the internet.[25] It contains accelerometers that measure the intensity of the wearer's movements and the built-in LEDs light up accordingly (Fig. 1.8). The latest developments include the construction of



1.7 Illuminating stretchable structure with built in LEDs.

1.8 Illuminating Twirkle shirt.

textile-based light-emitting materials.[26] TITV has made significant progress in integrating small LEDs in current textile production processes. In addition they have succeeded in achieving true illuminating textile structures by appropriate integrated fibres coated with the right semiconductive polymers in the right weaving configuration. This is in line with the PROeTEX document on fibre electronics. Challenges include selecting the correct materials and conceptual design, application of the coatings, and the materials themselves. Organic electroactive materials lack stability, high yields and range of properties. Consequently it is not possible yet to achieve a full colour spectrum.

1.3 European projects on smart protective textiles

1.3.1 Introduction

The European Commission has identified protective textiles as a lead market.[27] The Lead Market Initiative (LMI) is a European policy for six important sectors that are supported by actions to lower barriers to bring new products or services onto the market. Protective textiles is one of them, next to eHealth, Sustainable construction, Recycling, Bio-based products and Renewable energies. These markets have been chosen because they are highly innovative, provide an answer to broader strategic, societal, environmental and economic challenges and have a strong technological and industrial base in Europe. Also, they depend on the creation of favourable framework conditions through public policy measures more than other markets. Policy instruments are being developed dealing with regulation, public procurement, standardisation and supporting activities.

One of the first European projects on smart textiles for protection was the ICT project PROeTEX, funded under the Information and Communications Technology (ICT) scheme in the framework of the 6th Framework Programme. In 2009, the European Commission has launched a call on Personal Protective Equipment (PPE) within the Nanosciences, Nanotechnologies, Materials and New Production Technologies (NMP) window of the 7th Framework Programme. Eight projects have successfully passed the evaluation process.

1.3.2 PROeTEX

PROeTEX (Protective e-Textiles) is an FP6 funded European project on smart textiles for emergency workers. It is an integrated project, meaning that not only research but also implementation has to be considered. The project targeted research and development on materials for smart textiles for improved performance, textile sensors, communication through textiles,

1.9 PROeTEX inner garment.

development of prototypes including the electronic platform, feasibility study of fibre-based smart textiles such as piezoelectric textiles for energy scavenging and fibre transistors.

Three generations of prototypes have been built. They consist of an inner garment (Fig. 1.9) containing sensors that have to be in direct contact or near to the body: they measure temperature at the skin, heart and respiration rate, and the composition of sweat (detection of dehydration). Gas sensors are integrated in the boots. Most sensors have been built upon the results of previous EU projects such as Wealthy[28] and MyHeart[29] (textile sensors for measuring respiration rate and heart), and Biotex[30] (sensors for sweat analysis). The heart rate electrodes consist of knitted conductive textile structures; active respiration sensors have been achieved using piezoelectric materials. The sweat sensor is highly compatible with textiles, although not yet fully fibre based.

The outer garment (Fig. 1.10) includes another range of sensors: accelerometers provide information on the activities and position of the wearer (standing still, walking, running; upright or lying down), thermosensors indicate the risk of breakthrough of heat through the jacket, a GPS device provides information on the location (in open field, for instance when fighting fires in the forest). The outer jacket also houses an electronic box that controls data collection and processing, a flexible battery and an LED that turns red when a person is in trouble. All information is sent to a base station at the commanders' location via two textile antennae that operate in the Industrial, Scientific and Medical (ISM) band, enabling communication with a base station within a range of 10 to 100 meters. A flexible battery supplies the power. The inner and outer garments are connected via a wired link. Using the same technologies as the inner garment, a victim patch has been developed, consisting of a stretchable strap. Such straps are put on

1.10 PROeTEX outer garment.

each victim, enabling a distinction to be made promptly between victims in a stable situation and victims in need.

The PROeTEX project can be considered as the state-of-the-art suit in terms of smart protective textiles. The project finished in 2010. Before taking it into the market, more effort is needed to improve the robustness of several components and the system as a whole, to set reliable alarm values, in particular for instance for sweat analysis, taking into account physiological differences between people, and overall data processing. Indeed, the system should not increase the work load of the brigade, so information should be displayed only when action is needed, e.g. when a person needs to withdraw from the field or needs to be helped. Last but not least, the overall integration of the suit into the daily activities of the emergency worker needs to be carefully considered, in terms of battery charging, maintenance, connections, communication, etc.

As far as generic issues are concerned, the project started with an extensive definition of targets and product specifications. Also training, standardisation and exploitation have been important issues. Training addresses people involved in RTD, end users (rescue workers), users of the smart textile prototypes and the public. Two workshops were organised on sensors and actuators and on energy issues. Copies of the slides are available upon

request. A standardisation document has been established; it describes the standards in use, as well as the content of the CEN guidelines for setting up future standards on smart textiles. Also, relevant legislation, directives and regulation bodies are listed for various application ranges.

Within the PROeTEX project, attention was paid to gender issues. A gender policy plan includes activities by, for and about both genders. As rescue workers are predominantly male, the effort has targeted women. Activities *by* women concern involving women at all levels. PROeTEX was quite well balanced in this respect: a fair number of women were involved in project management, research, workshops, etc.

Research *about* women included the differences between men and women on physiological and mental levels. This is important knowledge for data interpretation and alarm settings. It also turned out that women were complaining that the suits did not fit very well, because their body shape is basically different. Good fit being important for proper functioning of the protection and monitoring, this may lead to injuries or system failure. Also for setting up procedures it can be worthwhile considering some differences: women tend to be more dexterous and careful whereas men are stronger. So it is useful to exploit these differences in a positive way.

Research *for* women was not considered at this point. At a later stage it could include the development of design guidelines for a suit matching their specific body shape and for men whose body ratios deviate significantly from the norm. In terms of improving comfort of protective suits, research could address active cooling for women at their menopause for compensating for hot flushes.

1.3.3 Other European projects on personal protective equipment (PPE)

At this moment, the PROeTEX suit can be considered as the state-of-the-art smart protective suit where a maximum number of components has been incorporated into textiles. Recent projects have started in 2010 and will last for three to four years.

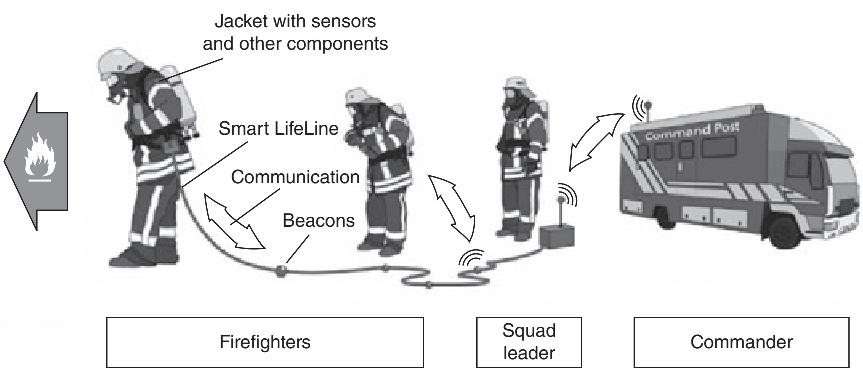
The *I-Protect*[31] project targets protection of firefighters, chemical and mine rescue workers. The selected solution will be based on fibre-optic sensors. Suitable technologies will be developed for integrating the optical fibres in the fabrics (underwear). Based on these, fabrics will be manufactured. Sensors will monitor man and his environment. Body parameters include respiration and heart rate, as well as body temperature. Regarding the working environment, targeted parameters are external temperature, concentration level of oxygen (O_2), as well as concentration of dangerous gases: CO, CO_2, CH_4, Cl_2, H_2S, NH_3. Conductive paths will be achieved through new functionalised carbon nanotubes suitable for application in

fabrics. New active indicators for end-of-service-life of PPE based on nanomaterials will be developed.

ProFiTex[32] follows a user-centred design approach: professional firefighters from an international group of firefighting services will be involved from the beginning in system design and evaluation to ensure that the system will meet their needs. To this end, ProFiTex will adopt and further develop the design approach developed in the European wearIT@work project. To mitigate the problem of unreliable wireless communication in building structures, ProFiTex will explore the approach of integrating into the lifelines used by many firefighting services, an innovative system for data transmission and tactical navigation (Fig. 1.11). This system will enable more robust communication between frontline firefighters and the rest of the command hierarchy. By monitoring several properties of the firefighters, such as their motion patterns and stance, problems can be detected immediately. The firefighters themselves are supported in their navigation in smoke-filled environments using infrared cameras and the positioning system implemented into their equipment. Firefighters will be able to store tactical information, such as the location of doors and victims, in their system in particularly easy ways. Information will be shared between the frontline firefighters, their group leaders and the rest of the command hierarchy outside the building. The amount and type of information supplied will be carefully chosen, considering the physical danger and psychological stress the firefighters are exposed to.

The *Prospie* project[33] aims at making a working prototype of a mobile, comfortable PPE that is effective in hot situations. The main targets are as follows:

- Phase-change materials (PCMs) and absorbing salts are tested and selected, based on optimal properties to cool and absorb sweat. Four existing cooling techniques are described in detail. PCMs will be



1.11 ProFiTex concept.

integrated to absorb energy during the temperature peaks. Evaporative water cooling will be combined with ventilation to cool in a continuous manner in the periods between the peaks of high temperature. Hygroscopic salts will be integrated to avoid an excess of humidity on the user's skin. Two designs for PPE are suggested. One is an overall with a homogeneous structure; the other uses different designs, depending on the body part. In both designs, evaporative cooling will be used to counteract steady high-temperatures between 40 and 60 °C and to provide cooling using PCMs to neutralise short high-temperature peaks of up to 150 °C.
- The selection of sensors, connectors and wiring systems will be based on state-of-the-art knowledge. Three stages are distinguished: a core system that can be easily achieved in Prospie, an extra system and an advanced system. The core system includes temperature, humidity and heart rate sensors. The functioning of the workplace sensors was shown to the Prospie community during the meeting in Magdeburg, December 2010. Heart rate, humidity, temperature and movements (accelerations) were monitored and made visible in graphs online. One external sensor, monitoring CO_2, was added.

The idea behind the *Safeprotex* project[34] is to create innovative solutions to address the main limitations of existing protective garments designated for rescue teams and emergency operators. Thus, the key scope of Safeprotex is to develop uniforms exhibiting the following characteristics:

- protection against multiple hazards,
- physiological comfort and enhanced mechanical parameters,
- extended service life compared to existing protective clothing.

In the frame of Safeprotex, three representative risky operations will be considered and corresponding protective uniforms will be developed as prototypes. More specifically, the project will address the following operations:

- emergency operations carried out in extreme weather conditions (floods, hail, etc.),
- operations carried out where there is a risk of wild land fires,
- first aid medical personnel potentially exposed to any type of risk.

The objectives are as follows:

- development and functionalisation of carbon nanotubes (CNTs),
- introduction of candidate fire retardant (FR) agents in layered silicates (LSs) modification,
- lab-scale production, evaluation and optimisation of master-batches incorporating CNTs, LSs, TiO_2 and chromic dyes,

- development of bi-component fibres incorporating phase change materials.

The main objective of the *Safe@sea* project[35] is to develop a new generation of advanced protective clothing for the fishing industry, leading to a significant increase in safety without reducing work performance. Targets are as follows:

- to develop new speciality and high performance fibres,
- to integrate lightweight and flexible solutions for buoyancy with ergonomic design,
- to integrate sensors,
- to integrate shock absorbing materials for head protection,
- to develop new clothing solutions based on fabric and design,
- to validate the proposed solutions for outerwear, gloves and head protection.

1.4 Protective textiles and comfort

Comfort is of particular importance in protective textiles. Protection often means wrapping the body with a cocoon that keeps threats outside; unfortunately it also keeps heat and moisture inside, possibly leading to discomfort after some time of use. On the other hand, protection from heat or cold, as well as from rain, snow and wind, is also an important area of protection. So here too comfort regulation is an issue. Smart textiles can also bring a solution to this problem.

Thermal comfort can be affected by the following factors:

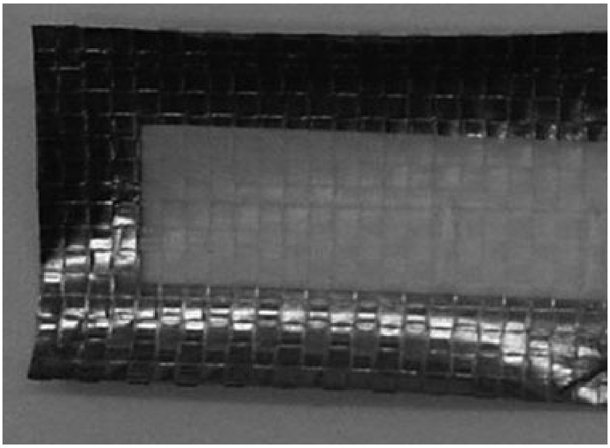
- heating or cooling,
- moisture and humidity,
- ventilation,
- insulation.

An adequate comfort regulating smart textile includes sensors and actuators, as well as accurate control strategies. As for sensors, the first question is which parameters are a reliable indicator of thermal (dis)comfort? Heart and respiration rate, sweat production, sweat composition, skin conductivity, and of course temperature, have been mentioned. As for ambient conditions, temperature, humidity and air current are determining factors.

In order to forecast how comfort is likely to evolve, context awareness is helpful: in which environment is the wearer? what is he doing? etc.

1.4.1 Sensors

Several sensors have already been described before in this chapter, such as ECG and heart rate sensors. Temperature sensors are usually based on



1.12 Temperature sensor by sputter deposition on PP woven substrate.

thermocouples. They are available in the form of wires and, as such, are already compatible with textiles. Work has been done to make them in a true fabric structure by sputter deposition (Fig. 1.12) or by coating at the fibre level (Prospie project, see Section 1.3.3). In the Biotex project, several principles for measuring the composition and properties of sweat have been studied.[36] They can also be used for humidity measurement.[37]

1.4.2 Actuators

Actuators can be used for

- heating,
- cooling,
- insulation,
- ventilation,
- moisture control.

Heating

Heating through textiles is fairly easy: a textile structure with the right level of conductivity suffices to exploit the Joule effect. Major challenges are homogeneous current distribution and supply of current. Several products can be found on the market, although not all of them use real textile structures but thin wires. Polar has presented a heating fleece.[38] It uses stainless steel fibres powered by regular batteries. Also Sefar commercialises woven heating elements.[39] Sioen has developed a heatable coverall. It uses heating

wires; energy is supplied by a rechargeable battery. The heating element resists multiple washing treatments in a washing machine at elevated temperatures up to at least 60 °C. The battery needs to be taken out during the cleaning treatment. It lasts up to 6 hours, depending on the level of power needed. Recharge time is 2 hours.[40]

Cooling

The Italian company Grado Zero has embedded ultrathin tubes in textile structures through which a cooling liquid can be circulated. An F1 pilot racer suit has been manufactured.[41] The liquid is cooled by a small Peltier element that is fixed at the back side of the suit (Fig. 1.13). However, all these systems are operated manually; this means they have to be switched on and off, and the level of heating/cooling has to be chosen.

Insulation

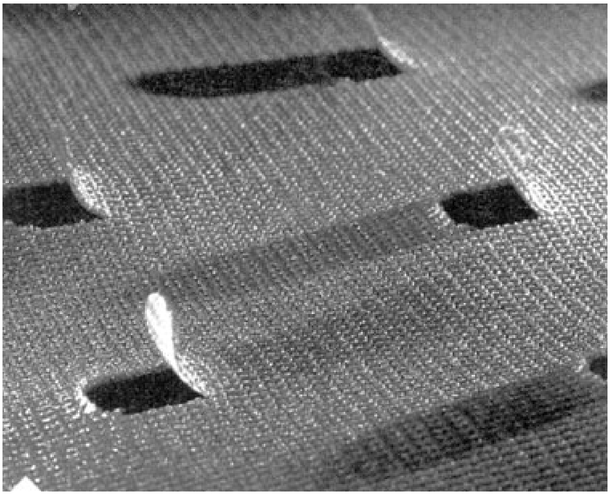
As conditions may change (temperature, intensity of activity, etc.), the need for insulation may vary as well. Adjustable insulation can be achieved by multilayer fabrics where the distance between the layers can be changed.

1.13 F1 driver cooling suit. The cool suits, helmets and backpacks are designed to fit with the look of the team and the West McLaren Mercedes race cars.

An example of such a product is an inflatable jacket where air has to be blown in to separate the layers by Oxylane.[42] Similar solutions are also used for generating floating capacity in marine clothes. Another product consists of a comfortable cotton inner layer and a heat-resistant aramid outer layer.[43] Shape memory springs separate the layers by opening up when a transition temperature is exceeded. This product is thin and comfortable at low temperatures, whereas at elevated temperatures it automatically provides thermal protection. At this moment, it acts only in one direction: the springs do not close when temperature drops again.

Ventilation

The most adequate way to achieve ventilation is by design. One concept has been presented for adaptive ventilating structures. Adaptable ventilation has been based on the structure of pine cones.[44] It consists of multiple layers having a large difference in hygral expansion coefficient. In a wet state the scales of the pine cone are closed. When the humidity decreases (in spring time), the scales bend away from each other and the pine cone opens, allowing the seeds to get out. Similarly, a multilayer coating is coated into a fabric. U-shaped perforations are punched in the fabric and coating (Fig. 1.14). When the material is wetted (simulating sweating) the blades of the perforations bend, creating a large ventilation effect. The system is fully reversible.



1.14 Adaptive ventilation based on pine cones.

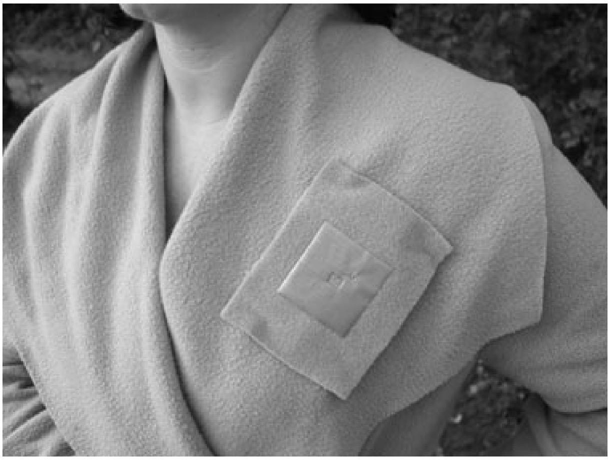
Moisture control

Moisture control can be achieved by appropriate choice of materials and design of the textile product. Some materials have been discussed already in Section 1.2.3. Materials such as gels and nanofibre structures[45] have huge absorption capacities. Of particular interest are smart gels that switch from hydrophilic to hydrophobic as a function of temperature.[46] They are a tool for collecting moisture until they are saturated; then they can release the absorbed liquid in a controlled way by changing temperature.

1.5 Other functions of smart textile systems

1.5.1 Communication

Communication ranges from communication within and between components to communication between the textile system and the user or another person. The wearer wants to have feedback on the recorded information. He may want to give instructions to the smart textile system, for instance regarding heating or cooling. Long distance communication can be handled by textile antennae. Such an antenna can operate in the ISM band (Bluetooth range) over a distance of 10 to 100 meters, depending on the environment. In the PROeTEX project, a micro patch antenna has been developed.[47] The antenna has been designed to operate in a textile vest; it does not suffer from bending, humidity or covering layers. Through communication with a laptop or a mobile phone, long-distance connections can be achieved. The antenna can be printed onto the textile susbtrate (Fig. 1.15). A wireless link for short distance connections has been developed using induction.[48] It can



1.15 Printed textile antenna.

be seen as the sun in the pyjama in Fig. 1.1. It can be used for energy transfer as well.

Textile displays have been discussed in Section 1.2.5. Several types of pressure-sensitive textiles can serve as a textile keyboard. They are commercially available.[49,50] More intuitive ways of communication have to be developed in order to reduce the mental load of communication.

1.5.2 Data processing

As for the hardware, data processing still needs to be handled by electronics. Flexible electronics are more compatible with the specific character of textile materials. Stretchable electronics have been developed within the framework of several EU projects.[51–53] The *Stella* project has developed the basic concept of stretchable electronic boards. An example is given in Fig. 1.7.

The *Place-it* project builds upon this stretchable platform. Organic electronics, and specifically organic opto-electronics, are currently a very popular research topic, covered both by universities and companies. The high intensity of research implies that the quality of organic opto-electronic devices will improve rapidly within the next years. Due to the freedom of shape, organic opto-electronic lighting has a clear advantage over other light sources.

The *PASTA* project will combine research, on electronic packaging and interconnection technology with textile research, to realise an innovative approach for smart textiles. By introducing new concepts for electronic packaging and module interconnections, a seamless, more comfortable and more robust integration of electronics in a textile will be possible. The main technological developments will concentrate on a new concept for bare die integration into a yarn (by means of micromachining), a new interconnect technology based on mechanical crimping, and the development of a stretchable interposer serving as a stress relief interface between the rigid component and the elastic fabric. The technologies will also be assessed in a functional evaluation and reliability testing program. The proposed solutions for integration of electronics into textiles will cover a whole range of components, from ultra-small LEDs to complex multichip modules. Moreover, a system design task will tackle the power distribution and system partitioning aspects, to provide a complete solution for integration of a distributed sensor/actuator system in a fabric.

Another step forward is the development of fibre transistors.[54–56] Woven structures provide the necessary flexibility for designing complex interconnections between a set of such transistor fibres. However, the quality and durability of such interconnections remains a huge challenge. Today, only very simple algorithms such as AND or OR ports have been achieved by

such materials and one can wonder whether complex data processing through textile fibres will ever be feasible.

1.5.3 Energy

Energy is an unresolved problem. Energy consumption must be optimised by a smart combination of distribution of tasks, energy storage and energy scavenging. As far as energy storage is concerned, two major concepts can be used, namely electrochemical storage and capacitive storage. Both suffer from a lack of high energy density, so capacity and volume have to be balanced. Today, flexible thin electrochemical batteries are available. They have been used in the PROeTEX suit. Capacitive batteries have been proposed, based on carbon nanotubes. They can be charged very quickly but the voltage supplied is not constant, in contrast to electrochemical batteries. None of the batteries can function properly when wet, so they have to be shielded from water.

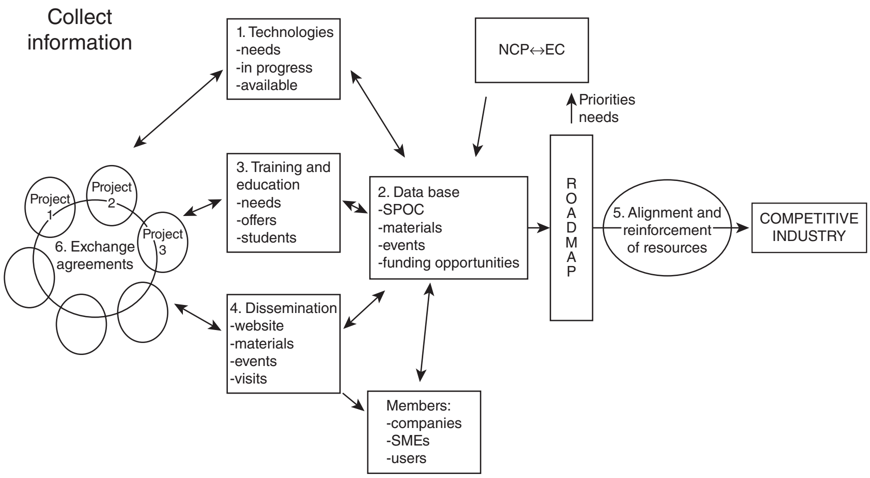
Energy can be scavenged from the environment using several principles:

- Photovoltaics in the form of textiles are the subject of the EU project Dephotex.[57]
- Piezo electric materials enable the conversion of elastic energy into electric energy;[58] in the PROeTEX project it was shown that the yield is very low.
- Infineon has developed a device that harvests electricity from body heat. It is based on the Seebeck effect.[59] The demonstrator developed by Infineon has the dimensions of a euro coin and produces enough energy for a small sensor. This means that a standalone sensor can be achieved by integrating a local thermogenerator together with the sensor.
- An electrogenerator can transform movement into electricity.[60] The generator consists of a planar coil, incorporated into both sides of the jacket, and permanent magnets in the sleeves. During walking, the magnets move relative to the coil, generating electric currents by induction. The power developed during one magnet motion is up to 5 mW and the generated energy is 0.8 mJ, which is sufficient to ensure a variety of health monitoring, sensor operation, etc.

1.6 Systex – a European coordination action for enhancing the breakthrough of intelligent textile systems

1.6.1 Objectives

The investment of the European Commission in research on smart textiles has already been highlighted. It is estimated that national funding in



1.16 SYSTEX project activities. SPOC, single point of contact; SME, small to medium enterprise.

European countries amounts from five to ten times the funding provided by the EU. A wide range of prototypes have been developed. However, these efforts have not been reflected, so far, in a significant number of commercial products; there is no real breakthrough. In 2008, the European Commission therefore decided to fund a project to find out where things were going wrong and what needed to be done to achieve the breakthrough: the Systex project.[61]

Systex wants to enhance the breakthrough of smart textiles by offering a supporting platform and by actively contributing to efficient RTD organisation and policy building. The project addresses four fields of application: protection, transportation, medical and sport. The project structure is illustrated in Fig. 1.16. The first objective is to collect relevant information in various areas on a worldwide level: scientific, technological, market related, training and education, people and companies involved, events and so on. About 100 research projects related to smart textiles are identified, most of them in Europe. Also non-technical information is gathered, such as white papers and market studies. Systex collects and provides material for training and education: courses, demonstrators, presentations, theses, etc. The information is available for members, via a web-based platform.

1.6.2 Policy building

Analysis of the available information allows identification of available technologies and products, as well as potential markets. From this analysis, needs for further research or technology transfer actions can be specified. This is part of the policy-building task of Systex. In a first phase, a vision paper has

been built for medical markets. It describes the drivers and barriers, weaknesses and strengths, as well as actions needed on short-, medium- and long-term basis.[62] By the middle of 2011, this had been further elaborated into a roadmap, including protective textiles as well.

System thinking

System thinking is being applied for understanding the dynamics of the smart textile market. The first step is to identify compelling needs and to make a priority ranking of potential products. Ranking is made based on the relevance for making this product a smart textile, the market size and the time expected for realisation. The system-thinking methodology analyses the topic as a system consisting of numerous events that affect each other in various ways.[63] It leads to a map of interlinked factors of which the interesting aspects are loops. Loops may connect in the form of feedback systems with positive or negative links. Positive links are enhancing the impact and this is what is looked for. Negative loops are balancing and damping. Eventually they can kill progress. Positive links show where actions should be focussed to be effective.

The targeted effect is put in the centre of the map. Heat stress protection has been identified as the key application. The next step is to find the factors that drive the use of heat-stress protection. Such factors are available funds, regulation, acceptance, procurement, etc. On the other side of the scheme are the effects caused by the use of heat-stress protection. Examples are reduction of casualties, positive stories, reduction of costs and so on. The last step of this phase is to find feedback loops that connect the effects to the drivers. Effects that are positively connected to a driver are the loops one is looking for: they allow one to enhance the dynamics of the system, i.e. they enhance the breakthrough of heat-stress protection.

Such schemes enable us to specify which actions are needed and which stakeholders need to be addressed in which way. The results of this exercise will be processed into a global recommendation document. Some preliminary conclusions are as follows:

- Benefits of using smart textile solutions must be considered carefully.
- There are no standards for testing specific smart textile components; directives, however, allow the set-up of guidelines on using smart textile solutions.
- Current procurement procedures do not foresee the option of addressing advanced innovative textiles; European actions must be taken for revising the procedures.
- User requirements must be the central focus; they can differ with country, type of brigade (city versus countryside) and type of interventions (building versus open area).

- Technology may not be mature yet; Systex has set up a four-phase plan evolving from low-end, short-term up to high-end long-term objectives offering realistic technological products.

Standardisation

Standardisation of methods for testing of smart textiles is a very particular problem. As it can be the marriage between, for instance, textiles and electronics, existing standards from the one sector are not necessarily suited for materials from the other sector. In the introduction, reference was made to standardisation activities at the European level. The current document established by the Working Group 31 of Technical Committee 248 of the European Standardisation Committee CEN on smart textiles provides a definition and classification of smart textile systems and their components. It does not describe test methods; instead, it addresses the aspects that should be considered when setting up a new standard for smart textiles:

- Intelligent textile materials and systems should meet the requirements of similar 'non-intelligent' textiles plus *specific requirements* linked to their particular properties.
- They should *not harm* the wearer or put him/her at risk.
- Cleaning or maintenance should have no adverse effect on the materials or systems.
- They should be marketed with a *product label* providing the necessary information to the consumer.

The document also indicates EU regulations of potential relevance and standardisation bodies of potential interest for a number of application areas.

1.7 References

1. Comité Européen de Normalisation CEN TC 248 WG31.
2. http://www.p4c.philips.com/files/l/levi_icd_jacket/levi_icd_jacket_dfu_eng.pdf.
3. http://magict-shirts.com/retail.html.
4. W Lotens, Methods to assess physical protection in an operational context, NATO Advanced Study Institute, *Defense Related Intelligent Textiles and Clothing for Ballistic and NBC (Nuclear, Biological, Chemical) Protection*, 6–16 April (2010), Split, Croatia.
5. L Van Langenhove, C Hertleer, Smart textiles for medical purposes, *MEDTEX 03, International Conference and Exhibition on Healthcare and Medical Textiles*, July 7–9th (2003), Bolton, UK.
6. http://www.smartex.it/uk/projects/physensor.htm.
7. http://www.medes.fr/VTAMN.html.
8. www.gtwm.gatech.edu/.

9. A Reho, Textile sensing in sports and medical areas, *Smart Fabrics Conference*, London, 4–6 April (2011).
10. M Catrysse, R Puers, C Hertleer, *et al.*, Towards the integration of textile sensors in a wireless monitoring suit; Sensors and Actuators A – Physical 114 (2–3): 302–311, September 1 (2004).
11. L Van Langenhove, C Hertleer, B Lanfer, Long-term behaviour of textile sensors, *Transactions of the Institute of Measurement and Control*, 29 (3–4): 271–281 (2006).
12. F Carpi, D De Rossi, Electroactive polymer-based devices for e-textiles in biomedicine, *IEEE Transactions on Information Technology in Biomedicine*, Vol. 9 (3): 295–318 (2005).
13. http://www.hitech-projects.com/euprojects/context/.
14. NATO ARW, *Intelligent Textiles for Personal Protection and Safety* (2006), edited by S Jayaraman, P Kiekens and A-M Grancaric, Springer, ISBN 978-1-58603-599-0.
15. NATO ASI, *Defense Related Intelligent Textiles and Clothing for Ballistic and NBC (Nuclear, Biological, Chemical) Protection*, www.springer.com/physics/applied+%26+technical+physics/book/978-94-007-0575-3.
16. E Wilusz, Intelligent textiles for military applications, *Smart Fabrics Conference*, London, 4–6 April (2011).
17. WL Gore, Adding function (modern high performance fibres), *Textile Month*, Vol. 3: 12–18 (2004).
18. BD Martin, J Naciri, MH Moore, DA Lowy, E Pehrsson, B Ratna, Conducting polymer 'nanogates' – Controllable diffusivities in thin films of novel tether-containing sulfonated polythiophenes, *Electrochemistry Communications*, 11, 169–173, January (2009).
19. M Inami, D Sekiguchi, S Tachi, Le manteau transparent! (Transparent Cloak!), Brochure of Demonstration at Laval Virtual 2003, *Laval Virtual 2003*, France, May 13–18, (2003) (downloadable at http://www.star.t.u-tokyo.ac.jp/projects/MEDIA/xv/oc.html).
20. http://www.youtube.com/watch?v=PD83dqSfC0Y&feature=related.
21. http://physicsworld.com/cws/article/news/24975.
22. http://www.air-vest.com/aboutus.htm.
23. V Koncar, F Boussu, Flexible displays on textiles for personal protection, in NATO ARW *Intelligent Textiles for Personal Protection and Safety* (2006), edited by S. Jayaraman, P. Kiekens and A-M. Grancaric, Springer, ISBN 978-1-58603-599-0, 65–88.
24. www.lumalive.com.
25. www.cutecircuit.com.
26. U Mohring, Fabric-based novel illuminations and their applications, *Smart Fabrics Conference*, London, 4–6 April (2011).
27. http://ec.europa.eu/enterprise/policies/innovation/policy/lead-market-initiative/.
28. Wealthy – Wearable health care systems, *IST Project FP6*, IST-2001-37778.
29. http://www.hitech-projects.com/euprojects/myheart/.
30. http://www.biotex-eu.com/html/projectinfo.html.
31. http://www.ciop.pl/21160.html.
32. https://www.project-profitex.eu/.
33. www.prospie.eu.

34. www.safeprotex.org.
35. http://www.safeatsea-project.eu/index.html.
36. http://www.biotex-eu.com/pdf/phealth07_sweatrate.pdf.
37. D Depla, S Segers, W Leroy, T Van Hove, M Van Parys, Smart textiles: an explorative study of the use of magnetron sputter deposition, *Textile Research Journal*, 81 (2011), 1808–1817. (Based on S Segers, *Smart Textiles: An Explorative Study of the Potential of Sputtering Deposition*, Master Thesis, Ghent University, 2010, http://lib.ugent.be/fulltxt/RUG01/001/458/763/RUG01-001458763_2011_0001_AC.pdf.
38. www.polartec.com/warmth/polarfleece/.
39. www.sefar.com/.../SEFAR-PowerHeat-heating-fabrics.htm.
40. Heatable Coverall, *Smart Textile Saloon: Prototype on Stage*, Ghent 21 April: 51–52 (2011).
41. http://www.gzespace.com/gzenew/index.php?pg = coolig&lang=en.
42. http://www.businessweek.com/innovate/content/jul2009/id20090729_919318.htm?chan=globalbiz_europe+index+page_special+report+–+design+awards+2009.
43. DA Russell, SF Elton, J Squire, R Staples, N Wilson, AD Proffitt, First experience with shape memory material in functional clothing, *Proceedings AVANTEX Symposium*, November 29, (2000).
44. http://www.asknature.org/strategy/1ebbd861249e5657c8c21b4fabe0d0f4.
45. B De Schoenmaker, L Van der Schueren, S De Vrieze, P Westbroek, K De Clerck, Wicking properties of various polyamide nanofibrous structures with an optimized method, *Journal of Applied Polymer Science*, Vol. 120: 305–310 (2011).
46. W Loos, S Verbrugghe, EJ Goethals, FE Du Prez, IV Bakeeva, VP Zubov, Thermo-responsive organic/inorganic hybrid hydrogels based on poly(N-vinylcaprolactam), *Macromolecular Chemistry and Physics*, Vol. 204 (1): 98–103 (2003).
47. C Hertleer, H Rogier, L Vallozzi, *et al.*, A textile antenna for off-body communication integrated into protective clothing for firefighters, *IEEE Transactions on Antennas and Propagation*, 919–925 (2009).
48. M Catrysse, R Puers, C Hertleer, *et al.*, Towards the integration of textile sensors in a wireless monitoring suit, *Sensors and Actuators A – Physical*, 114 (2–3): 302–311, September 1 (2004).
49. http://www.eleksen.com/.
50. http://www.plugandwear.com/.
51. http://www.stella-project.de/.
52. http://www.place-it-project.eu/.
53. https://projects.imec.be/pasta/node/1.
54. B Van Genabet, *Synthesis and characterisation of copper, polyimide and TIPS-pentacene layers in the development of a solution processed fibrous transistor*, Master Thesis, Ghent University, 2010.
55. A Bonfiglio, *et al.*, Organic field effect transistors for textile applications. *IEEE Transactions on Information Technology in Biomedicine*, 2005 **9**(3): 319–324.
56. TAO Xuyuan, *Systèmes Intelligents Integers aux Structures Textiles*, PhD Thesis, ENSAIT, 2010.
57. www.dephotex.com.
58. I Krucinska, M Cybula, L Rambausek, L Van Langenhove, Piezoelectric textiles: state of the art, *Materials Technology*, 25 (2): 93–100, July (2010).

59. http://www.future-shape.de/publications_lauterbach/BodyHeatAvantex2002.pdf.
60. J Blums, G Terlecka, I Gornevs, A Vilumsone, Jacket with electrical generator, *Smart Textile Saloon: Prototype on Stage*, Ghent, 21 April: 53–54 (2011).
61. Coordination action for enhancing the breakthrough of intelligent textile systems (e-textiles and wearable microsystems); *Coordination action funded in priority FP7-ICT-2007.3.6. Micro/nanosystems; Project Number: 224386*; website www.systex.org.
62. L Van Langenhove, L Rambausek, A vision on smart textiles: Systex, *Smart Fabrics Conference*, London, 4–6 April 2011.
63. http://www.youtube.com/watch?v=1nI8mGwZl7U&feature=related.

2
Types of smart materials for protection

N. FINN, CSIRO Materials, Science and Engineering, Australia

Abstract: This chapter reviews smart and high performance materials that are currently used in protective textiles or are being investigated by researchers for protective applications. Fibres with high strength, heat resistance, chemical resistance, and electrical conductivity are discussed. Materials with piezoelectric properties for sensing and actuation, phase change materials that absorb and release heat, and shear thickening fluids are briefly covered. Protective films and electrospun nanofibre membranes and their methods of manufacture are described, as are nanofibres derived from natural sources. Applications of carbon nanotubes are reviewed and some discussion is given of why the outstanding properties of individual nanotubes are not yet fully exploited in macroscopic assemblies as pure nanotube fibres or as composites with a polymer resin.

Keywords: smart material, sensor, actuator, nanofibre, carbon nanotube.

2.1 Introduction: smart materials for protection

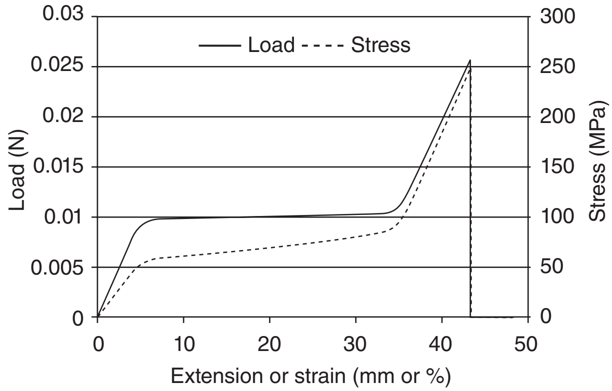
The field of protective textiles is both broad in its scope and very long in its history. Since early humans left the African savannah for colder climes they have sought better protection from the wide range of threats that they faced: cold and heat, rain and snow, sharp stones, thorns, spears, and knives. As technological development and scientific knowledge have progressed, so has the range of threats broadened and the means to guard against them developed. In the modern era, protection is sought against bullets, shrapnel, knives, viruses, bacteria, spores, energetic particles, electromagnetic radiation, sound waves, blast and shock-waves, extreme heat and cold, and toxic chemicals. The strategies used to protect against these threats include the recruitment of materials that provide barriers and those that can provide warnings; in the form of simple or sophisticated sensors. The range of material properties required is as wide as the range of threats. Often combinations of threats are expected and sometimes combinations of properties are needed to counter a single threat. This chapter describes the range of materials currently used in protective textiles, and looks at those currently being developed for the future. The textile structures that these materials are incorporated into are as important as the materials themselves and this

topic is also given some consideration. The performance of combinations of materials in composite structures is well known to be greater than the sum of the individual components and this will also be touched upon. Since fibres are the base unit of all textile structures, there is a focus upon the properties of materials in fibrous forms, which is also where unique properties that are not present in the bulk material or in particulate forms can be expressed and exploited.

The term ‘smart textiles’ can be defined as ‘textiles that can sense and react to changes in the environment, such as changes from mechanical, thermal, chemical, magnetic and other sources’ (Textile Glossary, 2011). A wider definition is possible as there are smart textiles for protection that actively sense threats and provide outputs for decision making or provide direct actions, and there are textiles that passively react to their changing conditions through their inherent properties. They can be considered to be equally ‘smart’: an ultra-high strength material that reacts to the impact of a high velocity projectile by passively dissipating its energy is as smart as one that changes phase to ameliorate temperature changes, or one that senses a toxic biological agent to provide a warning role. This chapter will therefore cover as wide a range as possible of smart materials, with a focus on fibres, but also on textile finishes, that can be or will be used in protective textiles.

2.2 High-performance fibres for protective textiles

High-performance fibres include carbon and glass, but these fibres are too stiff and brittle to be used in protective clothing and so will not be discussed in detail here. (The high modulus of glass and carbon fibres makes them very useful in fibre reinforced composites where stiffness in compressive loading is very important.) Man-made polymer fibres make up the majority of the textile fibres used in protective clothing (Hearle, 2004). Fibres are generally required to have maximum strength under tensile loading in the axial direction. The strength and modulus of a polymer fibre thus depends on the strength and degree of orientation of the molecular chains along the fibre axis. When a partially-oriented fibre is placed under axial tensile load, it stretches, and the tangled long chain molecules can slide over one another becoming mutually aligned, parallel to the fibre axis. As the orientation increases, the strength increases. Figure 2.1 shows a graph of the force and stress generated as a model partially oriented thermoplastic fibre is extended at a constant rate. The initial load generated at low extension is elastic and would be recovered if the extension were reversed. Beyond a certain point, known as the yield point, which marks the transition into what is called the plastic region, the fibre stretches with little increase in load as the molecules disentangle and become oriented. The fibre diameter is reducing during this



2.1 Superimposed load–extension and stress–strain curves for a model polymer fibre with low initial molecular orientation (a partially-drawn fibre, cold drawn in testing). [Note that the initial length was chosen as 100 mm so that extension (mm) and strain (%) are interchangeable in this example.]

stretching and the stress (dashed line) increases more rapidly than the load (solid line).

The slope of the dashed line in Fig. 2.1 provides the modulus (E):

$$E = \frac{\text{stress}}{\text{strain}} = \frac{\sigma}{\varepsilon} = \left\{\frac{\text{force}}{\text{area}}\right\} \bigg/ \left\{\frac{\text{extension}}{\text{original length}}\right\} \qquad [2.1]$$

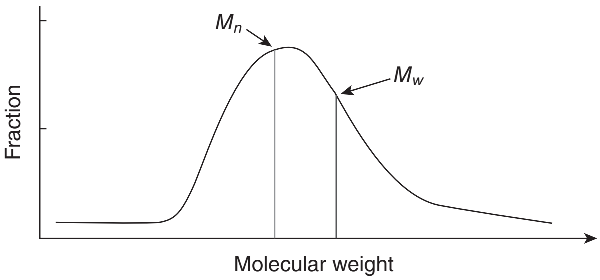
While the modulus that is usually reported for a fibre is the initial modulus at the earliest extension, the modulus can be defined at any stage in the stretching curve. It can thus be seen that the modulus increases as the orientation increases towards the end of the fibre's extension. The stress at which the fibre finally breaks is known as the tensile strength or ultimate tensile strength. If a fibre is supplied as a partially oriented material, then the strength may be defined as the stress at the yield point because the fibre is permanently deformed beyond that point. Strength without weight is the usual requirement for protective clothing and so strength for textile fibres is often described as tenacity: the breaking force divided by the linear density of the material. Units of tex (g/km) are used for the linear density of yarns and dtex (g/10 km) for fibres. The strength is often therefore defined in units of newtons per tex (N/tex), centinewtons per tex (cN/tex) or centinewtons per dtex (cN/dtex), where 100 cN = 1 N and 10 dtex = 1 tex. Fibres made from a material with low volumetric density (kg/m^3) have a larger cross-sectional area than fibres of higher density material at the same fibre linear density (dtex). The tensile strength and modulus expressed in terms of MPa thus may be lower for a low density material when, in fact, the strength per unit weight of that material could be higher. Researchers

and manufacturers of fibres tend to choose units that show their materials in the most favourable light but in protective textiles it is almost always the strength with respect to weight that is most important. If the strength in GPa is divided by the material volumetric density in g/cm^3 then the specific strength or tenacity in N/tex is obtained: if multiplied by 100, the tenacity is in cN/tex.

In order to facilitate the orientation of the molecules, a thermoplastic fibre is heated during manufacture while it is stretched. The vibration of the molecules generates more space between them, which allows their relative movement so that more uniform stretching and orientation can be achieved. The molecular vibrations also reduce the interactions between the molecules, hydrogen bonding and Van der Waals interactions, which also facilitates sliding, disentanglement and hence molecular orientation. When oriented side by side by drafting, molecules or segments of molecules can become highly ordered and form highly aligned crystals with a regular, very closely packed structure. The polymer is never completely crystalline and so is termed 'semi-crystalline'. The higher the degree of crystallinity, the greater the polymer density and the higher the fibre strength. The degree of crystallinity is usually defined as the ratio of the density of the semi-crystalline material under question to that of the purely crystalline form. Drawing is often applied to take the fibre close to the maximum orientation and crystallinity that can be achieved. If the drawing has approached the maximum achievable, then the fibre will be strong and have a high modulus, but will break at relatively low extension. If drawing is stopped a little earlier, then the fibre can stretch further under applied loads and more energy may be absorbed before failure, but the modulus is lower.

The strain energy absorbed in breaking the fibre is the force applied times the distance it is applied for, and so is equal to the area under the force–extension curve in Fig. 2.1. This can also be known as the *modulus of toughness*, or simply *toughness*, when the units used are energy per unit volume or Nm/m^3 which is the same as N/m^2 or Pa. The strain energy just to the yield point is called the *modulus of resilience*, or just *resilience*, because in the elastic region the stored energy is recoverable on releasing the strain. Those polymers that do not melt or that degrade readily with heat, are spun from polymer solutions in which the solvent separates the molecules and plasticises the polymer, in the same way that heat does for a thermoplastic. Solvent-spun fibres may be drawn as they are spun when the solution is dilute, or after spinning when the concentration has greatly increased through solvent removal.

The interaction between the molecular chains when they are aligned is also important for the fibre's strength. When any material is placed under load, the weakest part will fail first. The covalent bonds between atoms within the molecules are so great compared with the interaction between



2.2 Molecular weight distribution of a polymer.

molecules that the molecular interaction is the more important contributor. The most important, and simplest, factor in these interactions is the length of the long chains, which is related to the molecular weight. The molecules in a polymer do not all have the same molecular weight but range over a distribution, as illustrated in Fig. 2.2. The molecular weight for polymers thus usually refers to the average molecular weight but some properties also depend on the width of the distribution. There are several ways of calculating the molecular weight, the weight-averaged-mean is of most interest from the point of view of tensile strength and modulus because it is biased towards the heavier molecules, which have greater influence on mechanical properties.

The molecular weight can vary only in discrete steps of monomer weight. There are two main methods of calculating the average molecular weight for polymer engineering purposes. The weight-average-mean molecular weight is given by:

$$M_w = \frac{\Sigma_i^\infty N_i M_i^2}{\Sigma_i^\infty N_i M_i} \qquad [2.2]$$

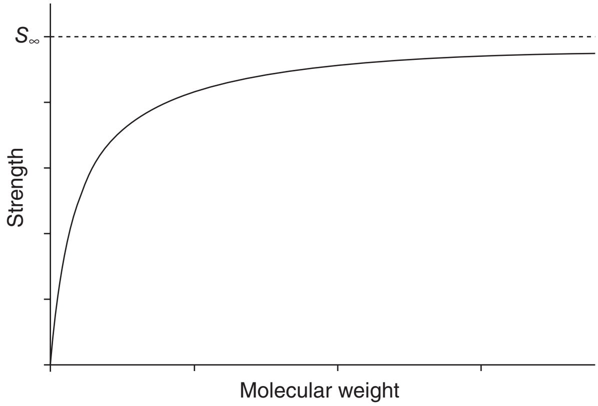
while the number averaged mean molecular weight is given by:

$$M_n = \frac{\Sigma_i^\infty N_i M_i}{\Sigma_i^\infty N_i} \qquad [2.3]$$

The tensile strength (and many other properties) depends on the weight-averaged molecular weight M_w in a manner described by:

$$S = S_\infty - \frac{A}{M_w} \qquad [2.4]$$

S is the strength and S_∞ is the strength at infinite molecular weight, while A is a constant and M_w is the weight averaged mean molecular weight. This is illustrated in the plot of Fig. 2.3, which shows that the strength saturates at very high molecular weight and is reduced at lower weights at a rate controlled by the constant A, which is different for each polymer. Many

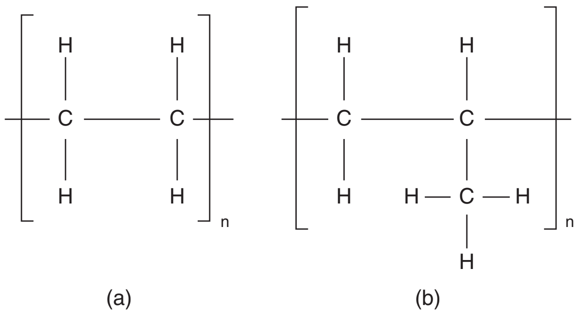


2.3 Dependence of strength on molecular weight follows a function of the form $S = S_\infty - A/M_w$.

other properties, such as thermal transitions and modulus, have similar dependencies on molecular weight.

Very high molecular weight provides high strength, and high molecular orientation, and high crystallinity provides even greater strength. To produce high orientation and crystallinity together with high molecular weight, certain difficulties must be overcome. In their very high molecular weight forms, common thermoplastic polymers such as polyester (polyethylene terephthalate, PET), nylon (polyamide, PA), and polypropylene (PP) cannot be thermoplastically extruded into fibres and properly drawn. Very high molecular weights are also difficult to achieve for polymers produced via a polycondensation process such as PET and PA (Volokhina, 2002). In these cases, post-spinning polymerisation must be performed in the solid state.

At very high molecular weights, the viscosity of the polymer melt is too high for conventional filament extrusion; attempts to extrude them result in frequent fibre breakages. Increasing the temperature to reduce the viscosity results in thermal degradation and chain scission, reducing the molecular weight and defeating the objectives of starting with high molecular weight. Some high molecular weight polymers can be plasticised with solvents and spun from a gel rather than from a pure polymer melt. The solvent is completely removed when the fibre has been partially drawn. Further controlled drawing steps at particular temperatures, speeds, and draw ratios give a pure polymer fibre of very high strength and modulus. However, at high molecular weights, most long chain polymers reach a limit of drawing due to the shape of their molecules, which causes difficulty with molecular disentanglement. An exception is polyethylene (PE) which has a very slender, straight chain, unbranched molecule and can be gel-spun and ultra-drawn to provide extremely well oriented fibres with very high strength and



2.4 Molecular structure of (a) polyethylene, (b) polypropylene.

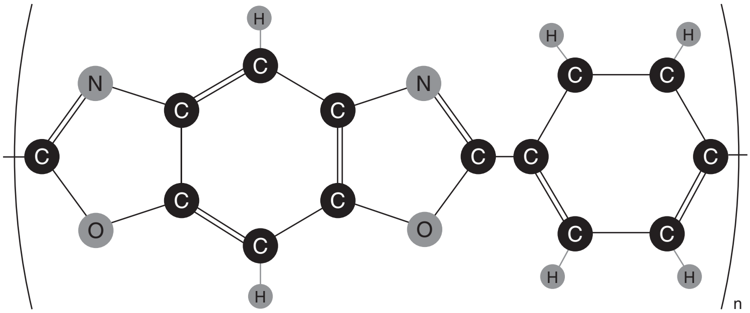
modulus. Polyethylene with molecular weights of several million can be successfully converted into highly drawn fibres. These ultra-high-molecular-weight polyethylene (UHMWPE) fibres were developed by DSM in the Netherlands and are marketed by them as Dyneema™ fibres. UHMWPE fibres are also manufactured by Honeywell in the USA as Spectra™ fibres. The low density of UHMWPE, at 0.97 g/cm^3, means that the specific performance is very high at 330 cN/tex for tenacity and 15 000 cN/tex for modulus (Sikkema, 2002).

Attempts to spin UHMW polypropylene and polyester have failed to produce high strength fibres, probably due to the irregularity of the molecular chains and the side branch (Fig. 2.4) which prevents close packing of the chains and affects drawing (Gregor-Svetec and Sluga, 2005).

An alternative method for achieving high strength and modulus is to produce rigid-chain molecules of relatively low molecular weight (20 000 to 40 000) with high alignment and crystallinity. The limits of drawing conventional polymers can be overcome by spinning polymers that are crystalline in the liquid state, otherwise known as liquid crystal polymers (LCPs). These polymers have rigid, rod-like segments containing benzene ring structures linked by flexible bonds. Examples of this type of fibre are the para-aramids such as Kevlar and Twaron, developed in the 1960s by Dupont in the USA and independently by Akzo Nobel in the Netherlands. These fibres are formed from poly-para-phenylene-terephthalamide, which forms the liquid crystalline state at high concentrations in a solvent (Sikkema, 2002; Vollbracht and Veerman, 1976).

Another example of a rigid-rod polymer is Zylon®, whose molecular structure is illustrated in Fig. 2.5. Zylon® consists of rigid-rod chain molecules of poly(p-phenylene-2,6-benzobisoxazole), otherwise known as PBO (Kitagawa, 1998).

Another fibre that exploits liquid crystal molecules is Vectran™. However, in this case the molecule is a polyester that has liquid crystal properties when molten and is extruded as a thermoplastic without the use of solvents.



2.5 Molecular structure of PBO, known commercially as Zylon®.

The melt-processing temperature is around 320 °C, requiring special extrusion equipment. Once fibres are formed, loss of strength begins at around 220 °C. Strength and modulus are high and chemical resistance is good.

The para-aramids, PBO, UHMWPE, and Vectran™ are commonly used in protective clothing for their high strength and toughness. Soft body armour is often made from these fibres where multiple layers of woven fabric can protect from low to medium velocity impacts of bullets or shrapnel. For protection from high velocity projectiles, rigid ceramic plates are incorporated into the garment but usually are used to cover only vital areas of the body because of their weight and stiffness. The ceramic plates fragment the high velocity projectiles and absorb and spread energy in doing so. The fragments of projectile and ceramic material are usually captured in a textile backing that may be adhered to the back of the plate. Often, the high tenacity, high modulus fibres are formed into a composite with straight fibres and no crimp to maximise the velocity of shock waves along them, spreading the energy over a large area in a short space of time. The impact of a high velocity projectile results in significant deformation of the ballistic composite on the body-side of the armour. While avoiding direct penetration of the body, this can lead to blunt trauma of adjacent tissues. The speed of sound in the fibre is dependent on its modulus – more specifically its dynamic modulus, which may differ from the quasi-static modulus.

These high toughness fibres are also used in fabrics for stab and needlestick protection, and have been incorporated into fabrics for anti-slash materials for public transport seating.

2.2.1 Heat resistance of high-performance fibres

In order for fibres to withstand high temperatures, they must be thermally stable, not melt or soften, and have high resistance to oxidation. For thermally protective clothing, the material must also be strong and durable, and when very high temperatures are encountered, reflection of infrared

radiation may also be needed. This is usually achieved by a thin metal coating applied to the outside of the fabric. The measurement that is commonly used to compare materials' resistance to burning in air is called the Limiting Oxygen Index (LOI). This is the minimum oxygen concentration (%) that will support combustion of the polymer. Very inert, incombustible materials require a high oxygen concentration to burn and so have a high LOI. Some polymers are inherently fire resistant, such as Nomex, PBO, Vectran, and PTFE, while others can be given enhanced fire resistance through additives or topical treatments such as viscose, wool, and polyester. The LOI of a variety of fibres is provided in Table 2.1 along with their mechanical properties.

2.2.2 High-performance fibres and yarns

High-performance fibres come in various forms and, for apparel applications, are usually formed into yarns. Fibres are available in various linear densities (dtex = g/10 000 m), as staple fibres in various chopped lengths for spun yarns or nonwovens (usually from about 30 mm to 65 mm), as continuous multifilament yarns, and as monofilament yarns. These can be formed into fabrics through weaving and knitting. Nonwoven fabrics from high-performance fibres are formed from staple fibres through carding or air-lay processes, followed by bonding. Conventional thermoplastic fibres may also be made directly into nonwovens from spun filaments in the so-called 'spunbond' and 'melt-blown' processes (Russell, 2006).

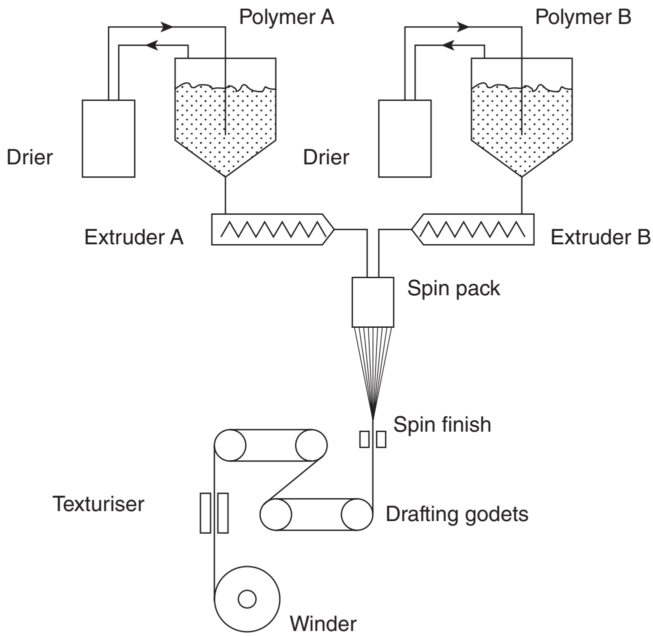
2.2.3 High-performance bicomponent fibres and microfibres

High-performance fibres tend to be made from a single polymer, but sometimes a combination of properties is required within a single fibre. In this case, blends of fibres can be used or bicomponent fibres can be spun. A bicomponent spinning system consists of two extruders feeding complex spinnerets that bring together the two different polymers in a process shown schematically in Fig. 2.6. Examples of the possible patterns within the fibre cross-section are shown in Fig. 2.7.

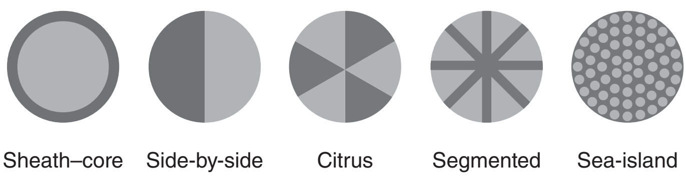
The simplest of these is the sheath–core construction, in which the two polymers are brought together at the spinneret so that one is injected concentrically into the flow of the other. The orifices in the spinneret are much larger than the final fibre diameter. High draft (stretching) occurs before cold-air quenching, but the original cross-sectional shape is preserved throughout the drawing process. Further drafting occurs on the heated godets, still preserving the cross-section. The sheath–core and side-by-side formats are most commonly used to make thermal bonding fibres in which

Table 2.1 Properties of high performance fibres

Type	Density (g/cm^3)	Tenacity (cN/tex)	Ext. at break (%)	Modulus (cN/tex)	LOI	Chemical resistance	Melt temp. (°C)	Operating temp. (°C)	Examples
Meta-aramid	1.38	41–78	25	840	30	Good		400	Nomex
Para-aramid	1.43	205–283	2.4–4.4	11990	25–28	Medium		230	Kevlar, Twaron
PBO	1.58	458	3.5	14170	68	Medium		370	Zylon
UHMWPE	0.97	327	3	15260	–	Excellent	120	100	Spectra, Dyneema
Vectran	1.4	266	2.8	9134	30	Very good		150	Vectran
PET (apparel)	1.36	35–50	25	800	–	low	260	140	
PET (tyre cord)	1.38	60–85	10	1060	–	low	260	140	
PA66	1.15	25–65	25	262	–	low	255	125	
PA (tyre cord)	1.15	65–90	23	700	–	low	255	125	
PA (ballistic)	1.15	90–106	23	709	–	low	255	125	
PP	0.95	40	25	–	17.4	Very good	165	80	
PP – Innegra ballistic	0.93	84	7	1646	–	Very good	165	80	Innegrity
PTFE	2.1	20	8.5	127.4	95	Excellent		288	Toray, Teflon
PPS	1.38	35–40	32–49	–	34	Very good		190	Ryton, Toray
Melamine	1.4	24	18	–	32	Medium		190	Basofil
PBI	1.4	24	27	400	41	Excellent		321	PBI Performance Products
PI (polyimide)	1.41	38	30	–	38	Good		260	P-84 (Evonic)
Carbon precursor		22	15	–	60	Low		256	Lastan(Asahi)
Carbon fibre	1.77	760	0.4–2.4	42000	–	Good		691	Toray, Hexel



2.6 Bicomponent fibre spinning.



2.7 Bicomponent fibre configurations.

one component is a low melting point polymer while the second polymer has a higher melt temperature. The fibres are formed into webs in nonwoven processes and later heated so that the one component melts and the fibres are fused together to form an often lofty resilient fabric, which can be used for thermal or acoustic insulation. The sheath–core construction can also be used where expensive additives are required only at the surface, or within the core, but not at both, or when the addition of functional particles is detrimental to strength. In the latter case, the additive can be placed only in the sheath or only in the core, leaving the second component to provide the strength or other desirable property. For instance, an antibacterial agent may be required only at the fibre surface. If used throughout the fibre, a large proportion of it would be wasted, while in a sheath–core

format it can be placed only in a thin sheath. If nanoscale particles are used that are smaller than the wavelength of visible light, then the particle-filled outer layer can be transparent and the colour of the fibre can then be determined by pigments in the core. This could be particularly useful in camouflage and infrared signature management.

Another example is when fine magnetic particles are used to make a magnetic filament or to absorb radiation at radio or microwave frequencies for camouflage or signature management. The particles are placed in the core where their magnetic behaviour is still apparent but the outer layer will dominate the colour of the filament, so long as the pigmentation is fairly dense.

Low melting-point metals or alloys, such as those used in solder, have been extruded as the core of a sheath–core fibre to produce fibres with very high electrical conductivity (e.g. Hills Inc., 2011).

The citrus, segmented pie, and sea-island types of fibre are used to produce microfibre fabrics or, in extreme cases, nanofibres. It is impossible to process ultra-fine fibres through conventional equipment because they form dense entanglements ('neps') and suffer high breakage rates. Therefore, it is necessary to make a bicomponent fibre whose total denier is conventional but which can be split down to microfibres later. The citrus and segmented fibres are usually mechanically split with water jets or needle punching, while in the sea-island fibres one component is dissolved away in a solvent in which the other component is not soluble. When first developed, an alkali-soluble polyester-based copolymer was used as the 'sea', with polyamide 'islands'. The dissolution process was relatively slow and difficult, requiring high pH and temperature. Recently, however, water-soluble polyesters have become available that can be melt spun and these are much more easily dissolved, and the resin is recoverable.

A conventional polymer may also be combined with an elastic polymer in a bicomponent fibre. This allows the development of elasticity in a nonwoven fabric by splitting the fibres, mechanically or chemically, after conventional processing. An elastic copolymer used as the low melt component of a thermal-bonding fibre for high bulk nonwovens also provides higher compressive resilience and durability compared with normal polymers.

2.3 Piezoelectric fibres, phase-change materials, and shape memory fibres

2.3.1 Piezoelectric fibres

The piezoelectric effect is the local redistribution of electric charge caused by imposing a mechanical stress on a material. If the rate of change of stress is high, a very high electric field can be generated. For instance, the

mechanical shock applied to a crystal of lead zirconate titanate (PZT) in a gas igniter generates many kilovolts per mm and sufficient current to produce an energetic spark in air. Some polymers, when in the right form, can exhibit the piezoelectric effect and this can also be enhanced by the addition of inorganic particles.

The polymer that shows the strongest piezo effect is a thermoplastic fluoro-polymer, polyvinylidine fluoride (PVDF), which can be processed into extruded fibres and films. Its use as a strain or motion sensing fibre is being investigated by several laboratories and it has also been considered for electricity generation in textiles. Piezo materials can also operate in the reverse mode, generating a stress when a voltage is applied to them, and so can be used as actuators as well as sensors. If used in a bicomponent structure with a non-active material, electrical stimulation can result in the bending of a sheet or a fibre. Stacks of film or bundles of fibres may generate quite strong actuation but it is only maintained while the voltage is applied and will then relax back to its original shape. The time scales for actuation and relaxation depend on the viscoelastic properties of the polymers involved, as well as the piezoelectric forces generated. The β-phase (of the four possible morphological phases: α, β, γ, and δ of PVDF) provides the maximum piezo- and ferro-electric effects. This is achieved by high drawing and orientation of α-phase material at elevated temperatures. The polymer can be polarised by electrostatic polling: immersing the material in a strong electric field while it is hot, enhancing the piezoelectric effect further.

While no commercial applications have yet been realised in protective textiles, there is much potential for piezoelectric fibres in this field, such as their possible use in the opening and closing of pores in protective textiles. Such a development could improve fire-fighters' outer layer, or Chemical, Biological, Radiological, Nuclear (CBRN) suits, which usually prevent transpiration of perspiration. In emergency use the fabric may need to block heat, smoke, dangerous chemicals, blood, or bacteria. However, the wearer suffers from thermal stress due to low water-vapour transmission rates and the low thermal conductivity of the clothing. To solve this issue, the piezo fibres may be actuated to open pores during rest or travel but be rapidly closed using an electrical pulse when required.

Another possibility is their use as a strain sensor for measuring impacts in ballistic protection materials. As a battlefield wireless network exists for modern soldiers, it would be possible for commanders to know when soldiers have suffered impacts, their locations on the body, and their severity. This could optimise the provision of medical assistance, as well as assist in the management of troops on the ground. A sensing application for use in sport is being explored at CSIRO in Australia. An electronic vest is worn by boxers that records and scores the impact and location of the blows

exchanged, eliminating the subjectivity that presently affects the judging of this sport. The vest also enables a new version of boxing to be developed which is for exercise only. Opponents are not allowed to land heavy blows but just tap their opponent. This involves much of the skill and fitness of boxing without the danger of serious injuries.

In principle, a piezoelectric composite material could be made to provide electrically controlled pressure in a garment. The speed of response could be high and so a garment might be designed to respond to movement, to enhance performance, or to prevent injury by limiting movement under extreme loads. With fast response, a garment could be designed to enhance performance and prevent injury by responding to, and limiting, movement under extreme loads.

PVDF is also thermally and chemically highly stable, and reasonably easy to process into melt spun fibres and extruded films. However, the degradation products from exposure to high temperatures in air can be extremely toxic.

2.3.2 Phase change materials

Phase changes occur when a material changes its physical state from a solid to a liquid or a liquid to a gas, or the reverse of these processes. These changes occur with a large transfer of energy, which is required to drive the transition or is evolved when it is reversed. The energy of the transition, specific to the material and varying with temperature and pressure, is called the 'latent heat' of that process. The energy of a melting transition is called the latent heat of fusion and that of an evaporating liquid is the latent heat of evaporation, and they are often expressed in units of kilojoules per kilogram (kJ/kg). The human body cools itself very efficiently by evaporating water (sweat), which requires about 2260 kJ/kg to do so. The rate of evaporation is driven by the difference between the saturated water-vapour pressure at the liquid surface and the vapour pressure of the air passing over it. The evaporation rate also depends on the speed of the air passing over the surface since this keeps the vapour pressure of the air at the surface to a minimum. The heat of evaporation of the sweat is supplied from the skin and so the body is cooled. Clothing prevents the passage of the water vapour and so reduces the efficiency of cooling. Solid-to-liquid phase change materials can be incorporated into textiles to provide some buffering of the temperature changes associated with exercise in warm clothing or by exposure to cold.

The human body perceives changes in temperature more sensitively than the absolute temperature. This feeling of discomfort evolved in early humans because it makes us change our environment to avoid overheating or overcooling.

The phase change materials used for clothing, such as Outlast™ technology, use waxy organic compounds whose melting points can be engineered to be close to the human body temperature of 37 °C and that have a high latent heat of fusion. Thus, when they melt, they require large amounts of energy without raising their temperature significantly. When the temperature drops, they re-solidify and give up their latent energy. This buffers severe temperature changes, slowing down the rate of change and making the wearer feel more comfortable. These materials are often microencapsulated in small particles to retain the molten wax.

A very large mass of phase-change material would be required to absorb significant amounts of energy, so the small quantity that can be incorporated into clothing can provide only a small buffering effect, reducing discomfort. There is insufficient heat absorption capacity available to absorb the heat generated by vigorous exercise and so prevent harmful heat stress. However, for moderate exercise in cold climates or in heavy protective clothing where the person feels cold in rest periods and may be too hot during exercise, they can enhance comfort.

2.3.3 Shape memory fibres

Shape memory fibres have the promise of providing textiles with sensing and actuation within the same material. The fibres in the textile are set in one 'permanent' form, usually with a physical restraint at a high temperature. The item may then be deformed and set in a second, temporary shape and, when later reheated, the material resumes the original permanent shape as if it had a memory of it, hence the name. The process may be reversible and so some materials could be switched between two states. In protective textiles this could be useful to indicate or act upon changes in temperature.

Shape memory polymers (SMPs) are often networks of two polymers having differentiated hard segments and soft segments that have different thermodynamic transitions, either glass transitions (T_g) or melting transitions (T_m). The material is first heated above T_{perm}, the higher transition temperature, which usually means that the polymer melts, and can be moulded or extruded. It is set in the desired first permanent shape, then cooled. When deformed at ambient temperature, the material is elastic. To set a second temporary shape the material is heated above T_{trans}, the transition temperature of the second component (lower than T_{perm}) and deformed to the temporary shape and then cooled to be set into that shape. When the original shape is required, the material is heated again to above T_{trans} but below T_{perm} and entropy-elasticity comes into play, forcing the material back to the original shape (Lendlein and Kelch, 2002).

Polyurethane is the prominent polymer used in this application, especially for fibres, because it has quite easily controllable transition temperatures and is simple to process. Meng *et al*., (2007) used poly(ε-caprolactone) diol-4000 (PCL) as the soft segment and isophorone disocyanate (IPDI) and a molecular extender called 1,4-butanediol (BDO) as the hard segment in polyurethane fibres. They both wet-spun and melt-spun this into fibres with shape memory capability and compared their properties. They showed that the melt-spun fibres were stronger and had better shape memory capability due to better phase separation in melt-spinning. This led to better crystallisation of hard and soft segments when compared with the wet-spun fibres.

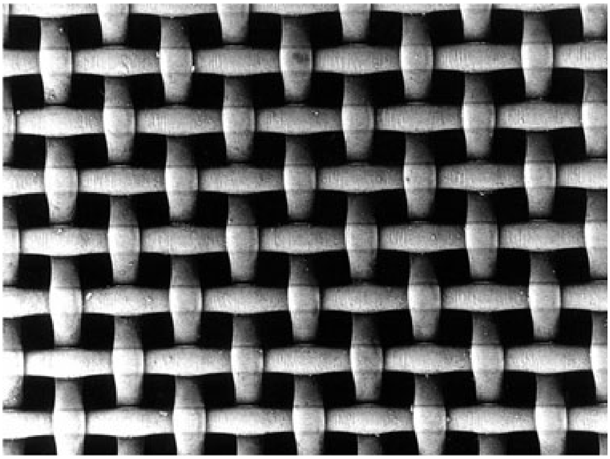
Recently, functionally graded shape memory polymers have been developed (DiOrio *et al*., 2011) but have not yet been applied to fibres. These materials allow a gradation of properties within one article so that different parts respond at different temperatures and this could be useful for actuation in protective textiles; for instance, opening the fabric when the wearer is hot but closing again rapidly when the outside temperature is dangerously high. Functionally graded materials have controlled spatial variation in their composition and hence in their function. In this example, a thermoset polymer's glass transition is controlled by spatially localised control of the temperature during curing through photo-induced cross-linking.

SMPs have been developed that will respond to stimuli other than heat, such as electricity, magnetic fields or light. Some SMPs can display two-way shape memory and even triple-shape memory (Lendlein and Kelch, 2002; DiOrio *et al*., 2011; Lendlein *et al*., 2005). Some of these use a nanofibre web showing SM properties embedded in a matrix also showing SM properties at a different temperature. This allows a second temporary state to be 'recorded' and reverted to with heating while further heating above the second transition temperature recovers the permanent state.

2.4 Woven and knitted structures for protective textiles

2.4.1 Weaving

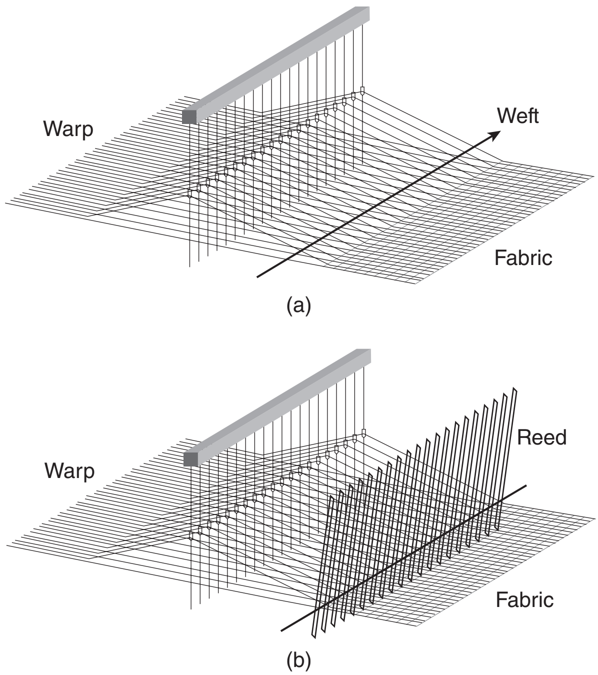
Woven fabrics are made from yarns by interleaving weft yarns through an array of warp yarns to form structures such as those shown in Figs 2.8 and 2.9. The weft yarns go across the fabric while the warp yarns run along its length. All weaving looms operate on roughly the same principles but may differ in the way that the weft yarn is inserted between the warp yarns. The weaving principle is that the warp yarns, which may number in the thousands across the fabric, are threaded through small holes or loops attached to wires called 'heddles' which are attached to movable 'shafts'. In



2.8 Woven fabric structure – simplest ‘plain weave’ structure using monofilament yarns.

2.9 Woven fabric in close-up, made from multifilament yarns.

its simplest form, alternate yarns/heddles are attached to either of two shafts so that when one shaft is raised and the other lowered, the yarns are separated, forming a space between then, as shown in Fig. 2.10a. Traditionally, the weft yarn is threaded through this open space (called the shed) between the separated sets of warp yarns, using a shuttle. In modern high-speed looms, the weft yarn may be passed from one steel rapier to another as they meet in the middle of the shed or it may be fired by a jet of air or carried by a projectile. When a shuttle is used it carries a bobbin of yarn that trails the weft behind it as it passes back and forth across the shed. The lifting of the shafts alternates so that successive weft yarns are trapped



2.10 Schematic diagram of the weaving process. (a) Shedding and weft insertion, (b) beating in. (The second shaft holding the unlifted warp yarns is omitted for clarity.)

between the alternating groups of warp yarns. The reed then beats the weft yarn tightly into the fabric, as shown in Fig. 2.10b. For more complicated patterns, groups of yarns may be threaded through groups of heddles attached to more shafts (Textile School, 2011). This allows groups of yarns to be lifted in a prescribed pattern. In addition, multiples passes of the weft yarn can occur for a single 'shedding' in the warp, producing more complex patterns such as twills. An advantage of the shuttle is that, in carrying its store of yarn along with it, the weft is not cut at the ends of the traverse but loops around, allowing closed tubes to be formed. The disadvantage of the shuttle is that it is very slow and a limited length of yarn can be carried, and so it must be regularly refilled with yarn. Changes in weft yarn type or colour require a change of shuttle.

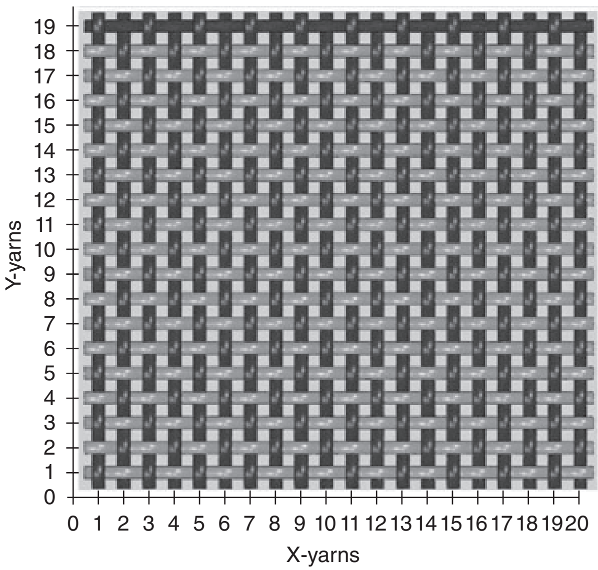
For very high strength fabrics, weaving is often preferred because the yarns are quite straight and take up the applied loads directly along their length. Because the yarns must deform around one another to form the fabric structure, they are crimped, usually in both directions. When extended in one direction (warp or weft), the yarns straighten and so increase the crimp in the orthogonal direction (weft or warp, respectively). Woven fabrics are less stable in the direction 45° to the warp of weft, this is called

the bias direction, and because neither set of yarns are aligned with the load direction, the force required to deform the fabric is reduced.

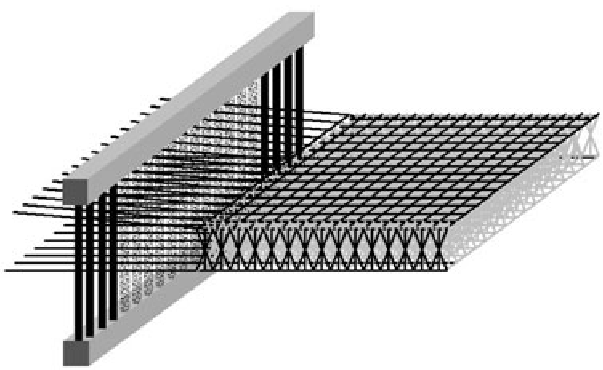
For applications such as ballistic protection, where high velocity projectiles must be stopped, the fabric is made up from many layers of woven material, usually using tough, high strength, high modulus fibres such as para-aramid or UHMWPE. For high velocity energy absorption, the most important factor, apart from strength, is the speed of sound in the fibres, because the shock wave of impact needs to be spread into as large an area as possible, as fast as possible. This requires high dynamic modulus. However, fibre toughness is also critical. High modulus fibres that are brittle, such as carbon or glass, would be of no use for ballistic protection because they fracture after extending only a small amount and so cannot effectively spread the energy of impact. Woven fabrics can also provide good protection against stabbing and cutting, but their low extensibility and poor elasticity make then stiffer than knitted fabrics and so not as comfortable to wear.

In most fabric sensing or electronic textile applications it is necessary to make electrical connections between yarns, sensing areas, or discrete electronic components embedded in the fabric. For clothing, it is desirable to use conductors that are as flexible as possible and to integrate them into the fabric rather than have them as added items that impact on the fabric mechanical properties in a detrimental way. If conductors are fully integrated, then woven fabrics can have the conductive yarns directed only along the warp and the weft; but this does lend itself to the classic addressable array in which sensing or actuation can occur at the cross-overs of the conductors. Single points can be addressed by selecting X and Y yarns as shown in Fig. 2.11. The problem with a simple woven fabric is that the conductive yarns would touch at every cross-over whether required or not, but this can be overcome by using double fabrics. By separating the warp yarns into two distinct layers, a double fabric can be woven on a single loom. With the appropriate number of shafts or Jacquard weaving, yarns can be brought from one fabric into the other in a particular pattern as required for the application (Fig. 2.12).

For example, yarns may be made from or coated with, a conductive polymer (e.g. polypyrrole, polyaniline, or PeDot (Skotheim *et al.*, 1998; Xue *et al.*, 2004; Bhat *et al.*, 2004)) or a thin film of metal which provides electrical resistance that depends on pressure when the two layers are pressed together. Alternatively, the electrical capacitance between the two layers of conductors within each face of the double fabric may be used. If the yarns bridging the gap between the two layers provide compressive elasticity, then a compression sensor can be formed. Since the spacing between the layers determines the capacitance and the spacing will depend on the load applied locally, then a fabric that can measure local pressure would be produced.

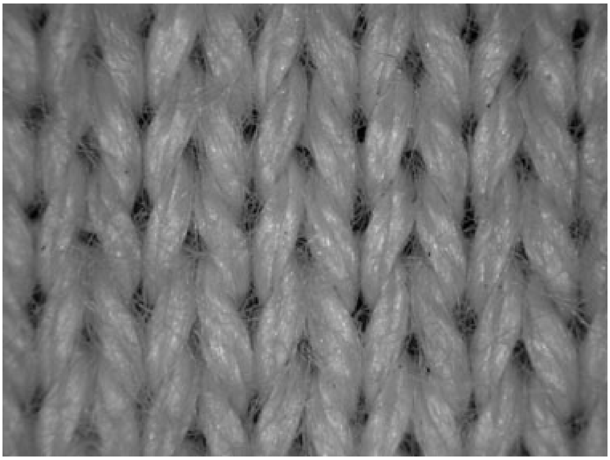


2.11 A woven fabric as an addressable electronic X–Y array.



2.12 Weaving a double cloth. Two sets of warp yarns and two or three weft yarns are used to form two connected fabrics in one operation.

Conductors embedded into woven fabrics can also act as aerials for wireless data transmission or to absorb microwave radiation to prevent detection by radar. For very high conductivity, metals are required, either as continuous metal filaments or as coated yarns. A commonly used metal-coated yarn is silver-coated nylon. The nylon yarns are coated from solution in an electrode-less plating process. These yarns are very strong, flexible and durable, making them well suited to textile applications.



2.13 Weft knitted single-jersey construction.

2.4.2 Knitting

Weft knitting

In weft knitting, a yarn is formed into loops that pass through a previously formed layer of loops using knitting needles. Each layer is called a course and the lines of loops along the fabric are called whales. The simplest weft knitted fabric structure is called 'single-jersey' and is illustrated in Fig. 2.13. This fabric is often knitted on a circular knitting machine in which a tube of fabric is formed in an efficient, high-speed process.

Knitted fabrics have great flexibility and elasticity, which leads to good comfort in apparel applications. They have some disadvantages in protective clothing in that they are generally weaker than wovens, and some knit structures can unravel when a yarn is cut, leading to expansion of holes. The looped structure means there are many small spaces between the yarns, that could allow ingress of particles and gases. However, by knitting appropriately dense fabrics and combining elastomeric yarns, these issues can be largely overcome. This trade-off between protection and comfort means that weft knitted fabrics have their place in protective textiles. Knitted fabrics can be described by the 'gauge' of the knit. This is determined by the needle density or spatial frequency of the machine used to knit the fabric and usually refers to the density in needles per inch. The needle density or spacing obviously determines the maximum density of loops in the knit but the loop length is also under the control of the knitter and this is fixed by the rate of feed or tension of the yarn as it goes into the needles of the knitting machine. Generally speaking, high gauge machines knit finer yarns into finer, lighter weight fabrics.

Whether from flat-bed or circular knitting, fabrics are traditionally cut up into panels and sewn together to form garments. For electronic textiles, this makes the job of connecting conductive yarns between panels difficult, but no more than for woven fabrics. A fairly modern technology called 'whole garment knitting' is a form of weft knitting where the stitch length, placement of yarns, and each individual needle is under complete machine control and double or quadruple sets of needle beds are used so that 3D shapes can be formed that fit perfectly to the desired form. Such knitting machines are manufactured currently by only two companies: Shima Seiki (2011) of Japan and Stoll (2011) of Germany. The 3D shape, usually a garment, is designed on a computer using special software that downloads the instructions to the knitting machine.

The yarns are also continuous and so conductive paths can be knitted into the fabric to place sensors or electrodes exactly where they are required. Dense complex fabrics can also be knitted that provide better protection from stab and needle-stick injuries while still allowing comfort and freedom of movement. This is of particular interest, for instance, in gloves, where tactile senses need to be preserved while protecting the wearer.

Metal filaments and conductive yarns can be readily knitted into complex shapes for garments that provide shielding for electrical safety when working on high-voltages. A conductive garment provides a Faraday cage for the wearer in which electrical potentials inside the cage due to charges at the surface cancel out to zero, so that no currents are induced to flow in the body of the wearer. It also provides a direct path for electrical currents around the body of the wearer.

Warp knitting

In warp knitting, as the name suggests, the warp yarns that run in the machine direction, along the fabric, are used to form connecting loops across the fabric. Thus warp knitting requires many more yarn packages compared to weft knitting for the same width of fabric. The warp knitting speed is high and the fabrics can have high elasticity and flexibility.

A wide variety of warp knitting styles is possible, including Tricot, Raschel, Milanese, and Crochet. Tricot and Milanese machines produce very elastic, flexible fabrics and hence are often used for lingerie production, support stockings and highly elastic sports-wear. Milanese produces fabric more slowly but it is more stable and stronger and so is used for more expensive items. Raschel knits do not stretch very much and have bulk in the thickness direction and are used for pile fabrics for coats and jackets. Weft insertion can be used with warp knits and this stops the fabric from stretching in this direction, making it stronger and more stable. Diagonal yarns can also be

2.14 An example of a warp-knitted spacer fabric, approximately 5 mm thick.

inserted and stitched into the fabric by the warp knitting needles to form very stable and strong multi-axial fabrics.

Warp-knitted spacer fabrics

Spacer fabrics are somewhat like the double-cloths mentioned in the section on weaving except that they are knitted and so have higher flexibility and extensibility. They are knitted on warp knitting machines with two beds and an extra mechanism to pass a second yarn, which may be of a different type to the main fabric yarns, across the gap between them. The density of the connecting yarns can be high so that quite a rigid separator is formed which can be used to absorb impact energy or to provide reliable separation from hazards, such as heat. An example of a warp-knitted spacer fabric is shown in Fig. 2.14. Other fibres and materials can be integrated into the warp-knitted structure in order to provide extra functionality. For instance, wool fibres have been mechanically combined for thermal insulation and fire resistance.

Shear thickening fluids have also been added to spacer fabrics to provide impact protection with greater flexibility. A shear-thickening fluid has low viscosity at low shear rates (low rates of extension or compression) but very high viscosity or rubber-like behaviour at high rates. A popular material with these properties is ‘Silly Putty’. This means an article could be flexible during normal movement but become more rigid when an impact occurs, which can be useful for sports applications but also has industrial uses.

2.5 Nonwovens

In nonwoven manufacturing, the fibre is converted directly into fabric without passing through a yarn stage. Although significant cost savings due

to the shorter process route make nonwovens attractive, nonwoven fabrics have inherent physical limitations and some advantages. These limitations and advantages can be understood through a comparison of the properties of wovens and knits with those of nonwovens.

Wovens and knits

- Within yarns: intimate fibre contact, helical fibre paths – strength and elasticity.
- Between yarns: looser linkages, yarn crimp.
- Drape, bulk, fluidity.

Nonwovens

Intimate fibre contact throughout is required to get strength and fibre security. This can lead to

- stiffness,
- poor drape – but high formability,
- fibres that are crimped and highly curved,
- poor stretch recovery.

The strength and elasticity of woven and knitted fabrics is provided by the yarns, the yarn crimp, and the yarn arrangement. This allows high fabric strength and good fibre security within the yarn while the fabric's flexibility and fluidity is provided by the looser links between the yarns. The fibres can be very straight and aligned with applied loads. Nonwovens cannot easily imitate this effect because the strength and fibre security of the nonwoven is derived from fibre entanglement.

The nonwoven process can be broken down into several stages:

(i) web formation,
(ii) bonding,
(iii) finishing,
(iv) colouration,
(v) converting.

In synthetic fibre nonwovens, the major web formation processes are as follows:

- carding (with cross-lapping),
- air-laid,
- wet-laid,
- spunbonded,
- melt-blown.

Fibres can be cut short into staple fibres or can be in continuous filament form. Web formation for staple fibre nonwovens can be achieved only by carding, air-laid, or wet-laid processes. Spunbond and melt-blown refer to high-speed, low-costs synthetic fibre processes, whereby fibres are

melt-spun and immediately drawn by high-speed air streams onto a suction belt to form a fabric. In the spunbond process, the fibres are well drawn continuous filaments of moderate linear density. In melt-blown, they are partially oriented finer fibres of finite length.

2.5.1 Cross-lapping

To produce heavier weight fabrics from a single card, a cross-lapper is often used. This device layers the light-weight web as it leaves the card so that the multi-layered web leaving the cross-lapper is perpendicular to the card direction. The ratio of the card speed to the cross-lapper output speed determines the number of layers and the weight of the cross-lapped web. In this case, the predominant fibre direction is across the fabric; the machine-direction to cross-machine-direction ratio (MD/CMD ratio) is then much less than 1.

The heavy cross-lapped web can be drafted, or stretched, to pull the fibre orientation towards the machine direction. Web-drafters use multiple, closely spaced roller-sets, moving at successively increasing speeds, to draft the web in several stages. In this way, MD/CMD ratios closer to 1 can be achieved but at the expense of fabric uniformity as the thinner areas tend to stretch more easily than the thicker regions.

2.5.2 Air-laid systems

Air-laid processes are an alternative to carding and cross-lapping. These machines use high-speed rollers and air-flows to generate a stream of staple fibres and air-lay them into a three dimensional web with high loft. The blending action in the air-laid machine is less than for a full nonwoven card as it has a small main cylinder, fewer or no workers, and little or no fibre recycling around the cylinder. However, the web properties are different to conventional card webs, having a more random orientation distribution and, in the high-loft version, many fibres arranged in the vertical plane compared with cross-lapped webs. This can give high vertical resilience and loft with high throughput speeds. The lofty webs are usually spray bonded or thermally bonded, but may be needle-punched or spunlaced. Production rates can be much higher than for the card-cross-lapper. As little blending and opening occurs in the air-laid process, greater attention must usually be paid to blending and opening prior to the air-lay machine.

For enhanced fibre orientation in the z-direction, another process that can be used is the ‘Struto’ or V-lap, vertical-lapping technology. In this case, a conventional card-web is folded or corrugated in the length direction and thermally bonded in that state.

2.5.3 Wet-laid systems

Wet-laid systems are similar to air laid except that the wet-laid means of fibre suspension is water rather than an air stream. The wet-laid system is also evident in paper making. The fibres are generally very short when compared with conventional textiles, falling into the range of 2 to 5 mm. These fibres are suspended in water at a rate generally below 0.005%, which is much lower than for paper making systems.

The web or batt is formed on a mesh or perforated belt, also known as a forming fabric, where the water is removed and the short fibres are distributed randomly. The forming stage is followed by pressing and drying for bonding of cellulosic fibres. Bonding for wet laid can also be achieved using the same methods as used for other nonwovens. These are chemical bonding with the addition of a polymer binder or by blending a low melt bicomponent fibre into the blend and later heating it. Wet-laid products have very low loft and often resemble paper in their physical properties.

2.5.4 Spunbond

The spunbond process extrudes thousands of melt-spun filaments and draws them in a high speed, ambient temperature, air stream, either all in one rectangular duct or grouped into a large number of round draw-tubes. The high-speed air draws the filaments, aligning the molecules with the fibre axis and also conveys them to a moving suction belt where they are laid down into a random arrangement and carried to a bonding station. Bonding is most often point-bonding through hot calendaring, compressing the filaments together with points on a hot patterned roller. Needle punching or, rarely, hydroentanglement is also used. The filaments are usually between 1 and 10 dtex.

Products of interest include medical gowns and drapes, components in chemical protection suits, clean-room clothing, and filters, usually with a barrier film or melt-blown layer for finer pore size. The polymers must be thermoplastics and the most commonly used are polypropylene and polyester, and occasionally polyamide (nylon). Bicomponent spunbond is also available with low melt polymers such as polyethylene and co-polyesters being common for sheath–core fibres. Co-polyesters and nylon are also used for sea-island fibres. The molecular weight distribution used is similar to fibres extruded for yarns and staple fibre production.

2.5.5 Melt-blown

In the melt-blown process, lower molecular weight polymers are used to provide low viscosity and high flow. The fibres are extruded into a hot, very

fast air stream that impinges on the fibres, immediately they leave the spinnerets. The fibres are drawn into fine filaments but the low molecular weight and high temperature drawing means that the strength is quite low. The fibres are collected on a belt or drum, with high suction to condense the mat into a fabric; some bonding occurs due to the high temperature when the fibres impact the belt. The melt-blown process is often used in combination with spunbond in a single process where a spunbond web passes under a melt-blown station and a finer web is formed in top of the first spunbond. The composite then passes through a second spunbond station to form a spunbond–meltblown–spunbond fabric (SMS). SMMS or SSMMSS or other combinations are possible. The fine melt-blown web provides small pores and good barrier properties while the spunbond layers provide strength and abrasion resistance.

2.6 Barrier films and nanofibre membranes

For full protection against the passage of liquids and particles, a barrier film is required and this is usually laminated to the fabric, which may be woven or nonwoven. If the film is completely impermeable, it provides a total barrier to liquids and particles but also causes discomfort to the wearer as water vapour cannot escape. In extreme cases, the prevention of heat loss through evaporation of perspiration can lead to serious heat stress. For instance, this occurs in fire-fighting apparel, or military CBR suits, where intense physical activity is required, but also leads to discomfort in less active areas such as surgical suites or clean-rooms. The films used as barriers are therefore often made to be microporous or water permeable through molecular diffusion.

One popular form of microporous barrier is super-expanded PTFE film (polytetrafluoroethylene, ePTFE), originally invented by the Gore company. A cast film of PTFE is stretched at high speed and, in so doing, it is drawn without the usual concomitant change in its external dimensions. Instead of necking or thinning as it is drawn, millions of tiny pores appear in the structure. The ePTFE material is inherently very hydrophobic and has one of the lowest surface energies of any material known. Liquid water thus cannot penetrate the pores but water vapour passes through relatively easily.

A cheaper form of barrier film is microporous polyethylene. The pores in this case are produced by embedding many tiny inorganic particles (often calcium carbonate) in the film as it is extruded. The film is later drawn and, as the inorganic particles cannot stretch, tiny holes appear around each particle. The pores are less numerous than in ePTFE and are also larger, providing less resistance to bacteria and viruses. PE also has low surface energy but not as low as PTFE and the barrier mechanism against liquids

is the same. Hydrophilic polyurethane membranes operate without pores and can completely prevent the passage of particles. Water vapour passes only by diffusion through the polymer after water vapour adsorbs onto the surface or liquid water wets it, but does not flow through. The diffusion rate is relatively low and so water vapour transmission rates are generally lower than for microporous membranes. The films vary in thickness from around 12 to 50 microns. Most of these barrier films provide hydrostatic resistance to more than about 10 m water-head pressure. Moisture vapour transmission rate (MVTR) varies from about 500 $g/m^2/24$ hr for a film with poor breathability to 4000 for one with very good breathability.

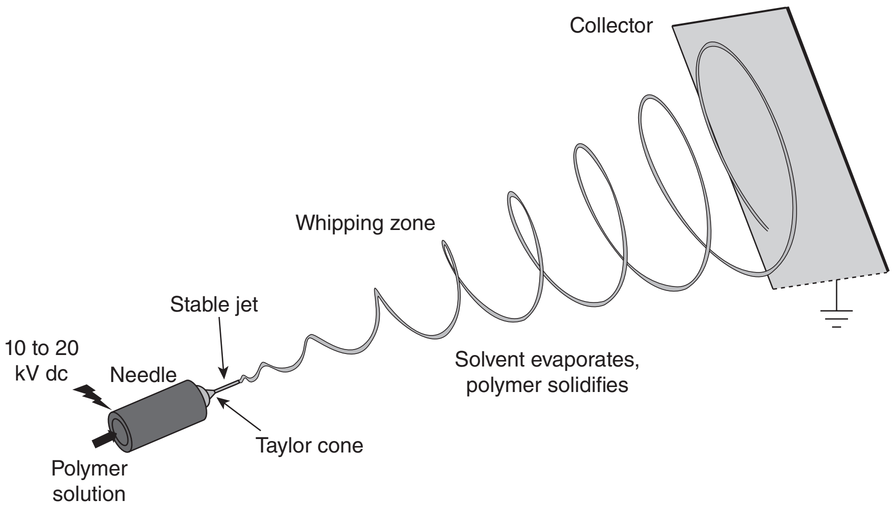
The benefits of using nanofibres in protective textiles are that their fine diameter means small pore sizes in fabrics or membranes, and very high specific surface area. The nanofibre fabrics are always nonwovens (at least currently) and are recognisable as fabrics only when studied microscopically. To the naked eye, and the human hand, they look and feel like continuous polymer films or membranes – only microscopic inspection reveals their fibrous nature.

2.6.1 Electrospinning

The diameters of electrospun fibres can range from a few tens of nanometres (1 nm = 10^{-9} m) to a few microns (1 μm = 10^{-6} m). The nanometre range is of most interest but micron-sized fibres can also be conveniently electrospun from polymers that are difficult to process in other ways or when, for instance, functional additives are incompatible with melt-spinning processes due to thermal degradation. The nanofibre membranes are most often used as barriers in protective textiles because of their small pore size but potentially can also be functionalised and used in textile sensors exploiting their high specific surface area.

The method of electrospinning was first discovered or invented in 1934 and, while it has been investigated as a fibre production process at some level ever since then, there has been a resurgence in interest and activity in the last ten years. This has included the first commercial exploitation of the technology by companies such as Elmarco in the Czech Republic, Donaldson Filter in the USA, and Teijin in Japan.

The principles of electrospinning are illustrated in Fig. 2.15 which shows a source of polymer in a solvent that is pumped to a fine needle, which is raised to a high d.c. voltage of between 10 and 30 kV with respect to the collector. The needle concentrates the electric field at the tip so that the field strength there is very high. A highly charged polymer stream is produced such that the ions and electrons in the fluid are partially separated to balance the strength of the electric field in the solvent filament. This generates a dielectric stress in the fluid, which stretches the stream but is



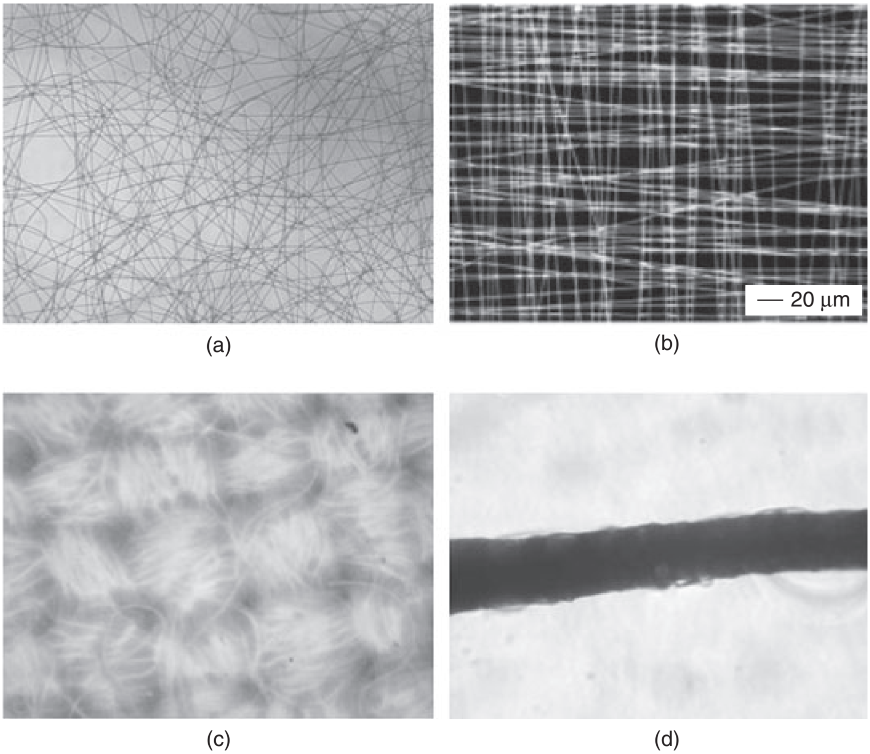
2.15 Schematic diagram illustrating the principles of electrospinning (laboratory scale).

also highly unstable. The stream is initially straight and parallel to the electric field lines. After travelling a small distance, slight variations in the shape of the stream result in an electrostatic force that increases the initial perturbation. This then interacts with the friction of the moving filament in the static air to reverse the direction repeatedly, and so produces a chaotic whipping motion of the filament. The extremes of the whipping motion in three dimensions describe a cone from the needle tip to the collector, whose shape depends on the voltage applied, the needle-to-screen distance, the viscosity of the fluid, and its flow rate. This process has been described theoretically and modelled by various authors.

The excess electric charge in the fluid filament means that each segment of it repels the adjacent segments in the axial direction, elongating the filament and leading to very high axial speeds, large draw ratios, and high degrees of molecular orientation. Most of the filament extension occurs in a plane perpendicular to the average motion of the material towards the collector, so that while the filament axial speed is high, even supersonic, the filament lengths between reversals are drifting fairly slowly sideways towards the collector, where they overlap to form a random web.

The viscosity needs to be controlled so that a fluid stream is produced that maintains its integrity while elongating; it must not break up into droplets but must not be so viscous that it cannot be drawn into ultrafine fibres.

Usually electrospun nanofibres are randomly orientated in the membrane or web, according to the whipping action as they are laid down (Fig. 2.16a). However, by moving the collection plane with respect to the



2.16 Nanofibre membranes. (a) Randomly oriented, (b) highly aligned, (c) on knitted substrate, (d) a nanofibre yarn.

jet, the fibres can be highly orientated. This is shown in Fig. 2.16b, where the collector was first moved in one direction and then moved in the perpendicular direction. This arrangement allows stiffer membranes to be made with tailored directional properties. The membranes can also be deposited onto a woven or knitted fabric (Fig. 2.16c), where the fabric structure can provide a template for the nanofibre lay-down pattern, producing membranes with engineered density patterns. Nanofibres can also be deposited onto nonwoven substrates. The nonwoven provides mechanical strength to lightweight electrospun membranes with very small pore size. The composites formed are used as filter media that can withstand a significant pressure drop, and durable barrier fabrics for protective apparel applications. With a suitable collector, the web can be rotated away from the collection zone and twisted into a yarn. This is shown in Fig. 2.16d for nanofibres spun from polyacrylonitrile (PAN) dissolved in dimethylformamide (DMF). Production rates are very slow and there is currently no commercial production of such yarns.

Fibres may also be electrospun using molten thermoplastic polymers that solidify as they travel to the collector. One advantage is that the use of solvents is avoided. Solvents may have occupational health and environmental issues, and their recovery and recycling adds cost and complexity to the system. Aqueous solutions of polymers also usually avoid these issues but very few polymers of interest are water soluble. A limited range of polymers can be melt-electrospun because the polymer viscosity needs to be within a very narrow range for fibre drawing and also depends on its temperature, which is difficult to control for nanofibres travelling through air. The spinning must take place in a temperature-controlled chamber to allow the fibres to be fully drawn, and where air-flows and especially convection currents are managed to avoid disruption of the filaments.

The main problem with electrospinning is the extremely low production rate. Single needle systems produce only milligrams per hour, which renders them useful only for research purposes. While multiple needle systems have been built, they still have very low production rates and are over-complicated, with inherently poor reliability and complexity. One commercial system that overcomes this issue is from the Elmarco company of the Czech Republic. Their system, illustrated in Fig. 2.17, uses a rotating drum that sits in a bath of polymer solution and to which the high voltage is applied. A film of solution is lifted onto the drum as it turns, and any random fluctuations in the film thickness grow under the action of the electric field so that multiple Taylor cones form over the surface and multiple filaments stream from the drum onto the collector. The substrate, usually a fabric, runs above the roller so that it is continuously coated with the nanofibre membrane. While providing much higher productivity than a needle system, multiple drums are required for higher speeds. Machines up to 1.6 m wide are available with speeds up to 10 m/min, depending on the nanofibre web weight

2.17 Elmarco Nanospider system (0.5 m wide laboratory device).

required. A melt-spinning system is also under development but details have yet to be released.

2.6.2 Centrifugal spinning

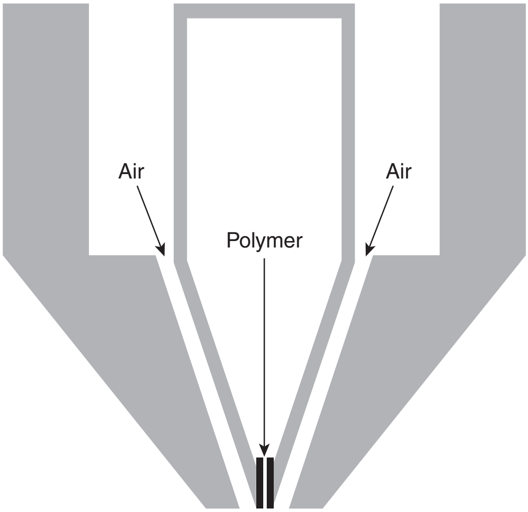
Another, less popular, method for producing fibres, in some cases nanofibres, is centrifugal spinning whereby the extruded polymer is extended by applying a strong uniform acceleration through high-speed rotation. The fluid may be a solvent–polymer gel or a molten polymer. Precursors for inorganic fibres can also be spun in this way. In one variant of the technology, an inverted cup is rotated with polymer chips injected onto a disc within the cup and rotating with it. The chips are thrown from the disc and then their inertia holds them against the rapidly rotating wall which is inductively heated to melt them. A polymer film forms on the wall and runs down to grooves at the edge of the cup that replace the spinnerets of conventional spinning. Filaments form at the grooves and are collected below, after high-speed drawing. The very short residence time means that delicate polymers that are sensitive to thermal degradation can be spun easily. The absence of spinnerets means that particles which would normally block the orifices can be more easily combined with polymers and spun into fibres.

With higher rotational speeds and pressurised extrusion, nanofibres can be formed. A recently commercialised technology exploiting this method is called 'Force spinning'. This method uses melt spun polymers or solvent systems and produces a relatively wide distribution of fibre diameters, with a mean around 300 nm when using polyethylene oxide (PEO) in water at about 5000 rpm (Fiberio, 2011).

2.6.3 Melt-blown nanofibres

The melt-blown process is a very common process for producing moderately fine fibres (a few μm in diameter) in nonwoven webs, but it can be modified to produce nanofibres from thermoplastic polymers at quite high production rates.

The polymer extrusion die is shown in Fig. 2.18 and consists of a row of multiple fine orifices through which low viscosity (low molecular weight) polymer is injected. The V of the extrusion die sits in a corresponding hot-air die such that the very high speed, uniform and symmetrical air flows pass down either side of the extrusion die and draw the filaments to great length and low diameter. The fibres are collected some distance away on a suction belt or drum where they are compressed into a mat. The fibres are not continuous but are very long compared to staple fibres. The fibres may still be soft when they are collected and some adhesion may occur, but

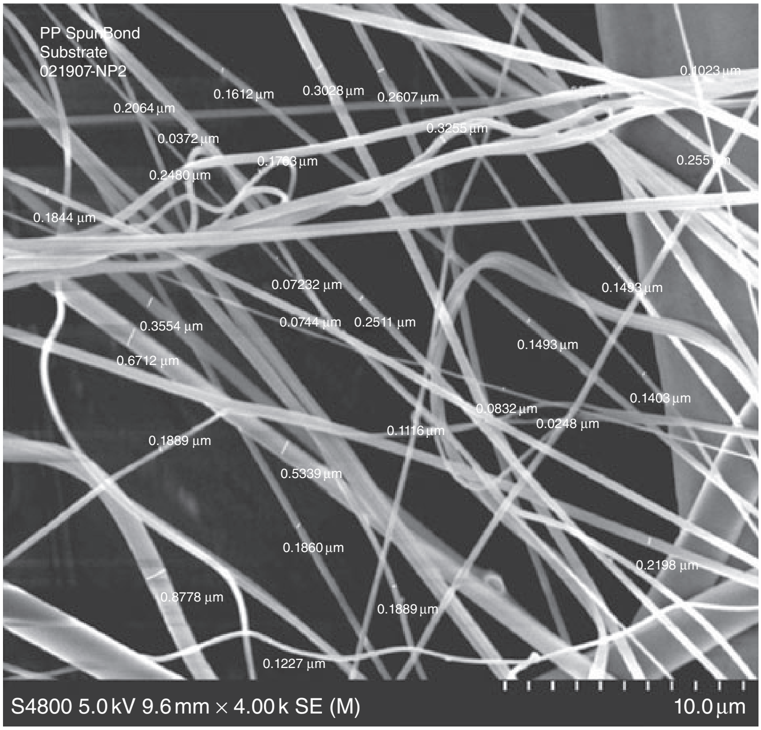


2.18 A melt-blown polymer extrusion die in cross-section. The die has a large number of round orifices across its width, through which polymer is extruded. The high-speed hot air exits from a continuous slot parallel to the orifices, or from concentric orifices, and draws the fibres while propelling them to the collection belt. The die extends to the width of the fabric.

mostly the web is held together by entanglement. The fibres from common melt-blown systems are fine, at a few microns in diameter, but not nanofibres.

Recently, Hills Inc. (2011) of the USA developed a melt-blown nanofibre system that uses low molecular weight polymers with narrow molecular weight distribution and high melt-flow index. Very precise dies and well controlled air flows allow the production of nanofibres with a distribution as shown in Fig. 2.19. The apparently very thick fibres in the background are the 20 μm spunbond fibres of the substrate material. The average fibre diameter for the melt-blown component is 250 nm and, in this case, they were spun from PBT polymer. The production rate was around 3 kg/hr/m width, which is greater than the other methods of nanofibre production. The disadvantage is the width of the diameter distribution and the limitation to thermoplastic polymers. The melt-blown fibres are also quite weak and have low abrasion resistance. Their use is mainly for filtration and breathable barrier applications. The pore size of a spunbond fabric is too large to prevent the passage of small particles such as viruses and bacteria.

In disposable medical gowns and drapes used for surgery and sterilisation wrappings, a melt-blown layer is often sandwiched between two spunbond layers to provide improved barrier properties while allowing the passage of water vapour when the wearer sweats; also the ingress of steam or gases

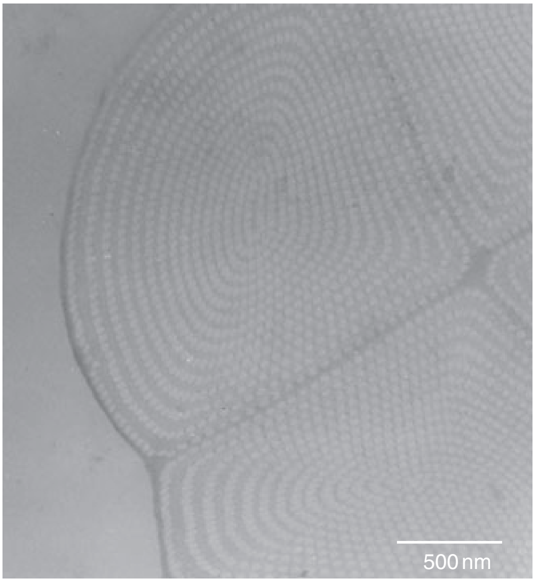


2.19 SEM image of melt-blown nanofibres (Hills Inc., 2011).

for sterilisation. In normal, coarser diameter, melt-blown fabrics, the pore size is still too large to stop viruses and spores.

2.6.4 Sea-island nanofibres

Sea-island fibres are bicomponent melt-spun fibres where a multitude of subfilaments of one polymer (islands) are extruded into a second polymer (sea) and then drawn as usual into fibres (see Fig. 2.7). If single microfibers were spun in the usual way then it would not be possible to process them via conventional textile routes because they would break, entangle, and form so-called neps, giving very poor quality products. The sea-island process allows the composite fibres to be processed into fabrics at normal fibre diameters then the 'sea' polymer is later dissolved away to leave the microfibres. In some cases, a very large number of sub-filaments are spun in each filament, up to 1000 per fibre. The resulting fibres are drawn in several stages so that the sub-filaments are reduced to nano-scale dimensions. The Teijin company of Japan have developed a rapid heating process in which an infrared laser locally heats the polyamide-polyester fibre very



2.20 Teijin sea-island fibre in cross-section, showing nanofibre subfilaments (Nakata *et al*., 2007).

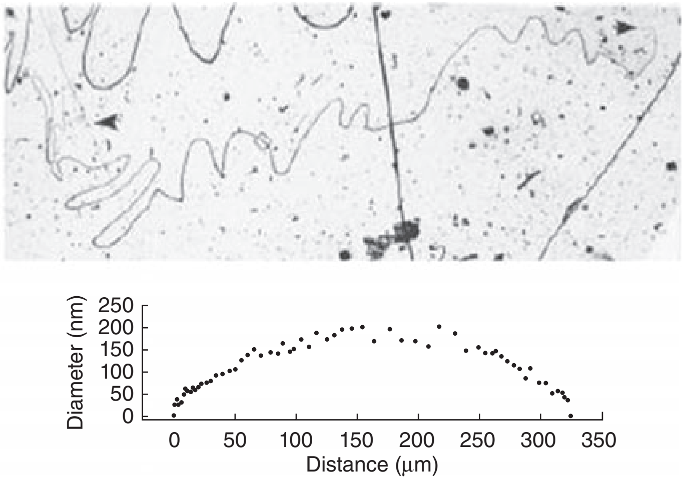
rapidly over a small region, which allows high ratio drawing followed by rapid quenching to produce fibres with diameters less than 100 nm (Nakata *et al*., 2007). (Fig. 2.20)

2.6.5 Naturally occurring nanofibres

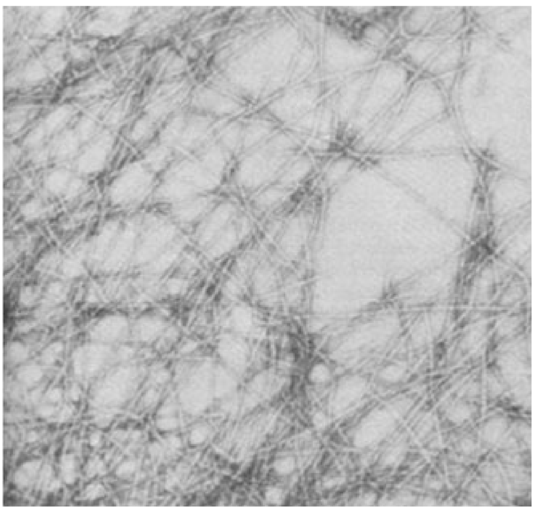
Although nanotechnology is fairly new to humankind, nature has been exploiting it for a very long time. A wide variety of natural nanofibres exist in nature and some of them have potentially useful properties that may be exploited if they can be produced in sufficient quantities in an environmentally and ethically sustainable manner.

One natural nanofibre is collagen, which is found in many animal tissues where it provides strength and elasticity. Fig. 2.21 shows an electron micrograph of a stained sea urchin fibril by Kalder *et al.* (1996). The ends of the fibril are marked with arrowheads. The graph shows the variation in diameter along the length of the fibril, showing that it ranges from about 20 nm at the ends to 200 nm in the middle.

Keratin is the protein that forms most animal hairs and horns. Animal hairs are complicated structures, having an external cuticle and intermediate filaments within them. It is possible to isolate the intermediate filaments and measure their dimensions and properties. This has been done by Jones (1975), whose image of intermediate filaments from rat's whiskers is shown



2.21 Collagen filaments from sea urchin ligament (Kalder *et al.*, 1996).



2.22 Keratin fibre intermediate filament isolated from rat's whiskers. (Reprinted from *Biochimica et Biophysica Acta (BBA) – Protein Structure*, Vol 412, L. N. Jones, The isolation and characterization of α-keratin microfibrils, pp 91–98, Copyright 1975, with permission from Elsevier.)

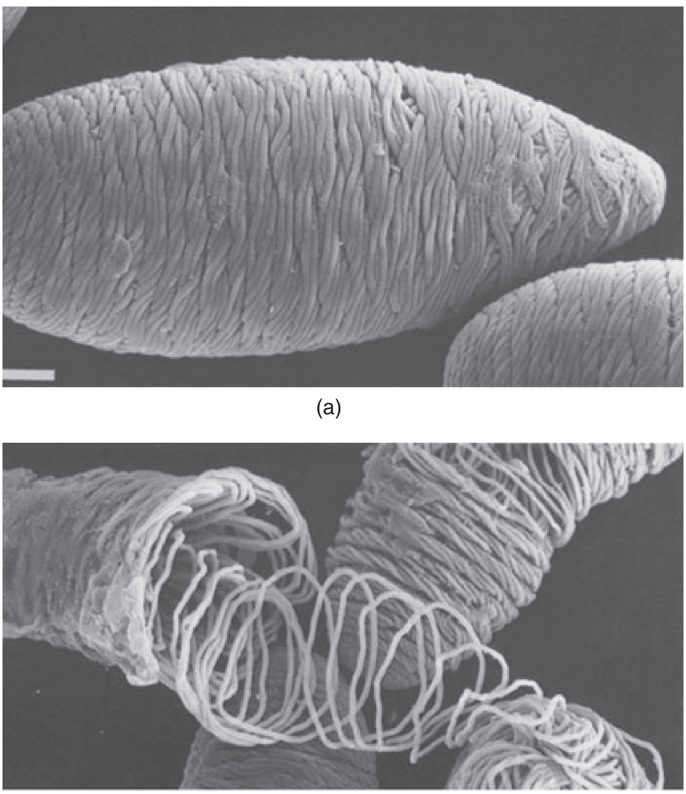
in Fig. 2.22. The intermediate filaments are nano-scale fibres of highly crystalline keratin and have high strength.

Fibrin is a protein fibre polymerised from fibrinogen that causes blood to clot; it does this by forming nanofibres that link together to form a solidified matrix that closes off the blood flow. The fibrin in a blood clot has a

diameter of around 100 nm. A human or bovine blood-derived form of fibrin is used with thrombin to make 'Fibrin Glue', which is used in surgery as a topical adhesive and sealant for assisting in a variety of procedures including skin grafts, closing fistulas, sealing wounds and delivering drugs and genes.

The hagfish is an unusual animal as it secretes copious quantities of a slime as a protective mechanism when threatened by predators. The slime consists of a dilute solution of mucus, and bundles of intermediate filaments of about 10 nm diameter, in sea water.

Figure 2.23 shows an electron micrograph of hagfish slime threads (Downing, 1984). Much work has been done by biologists on the properties of intermediate filaments, and hagfish slime offers researchers a relatively large quantity for study compared with that available in normal cells, as well as being of interest in its own right. The hagfish slime threads are composed of many nanoscale intermediate filaments bundled together and



(a)

(b)

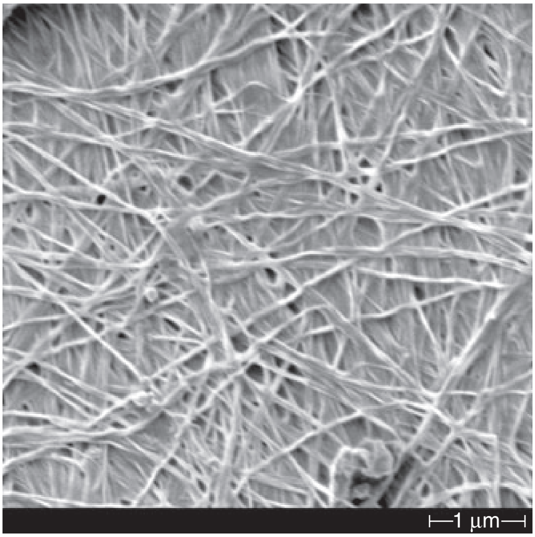
2.23 Hagfish slime thread intermediate filaments (scale bar = 20 μm) (Downing, 1984). (a) Bundled intermediate filaments; (b) intermediate filaments released.

are assembled within specialised gland thread cells into the rolled beads, as shown in Fig. 2.23. The cell is almost entirely filled with these threads, which are self-assembled from proteins expressed by the cell. How they are assembled into the bundles and coils is a mystery. When released, the coils unravel and a cloud of slime is produced that protects the fish from an attacking predator by blocking the attacker's mouth and gills. Many predatory fish use mouth suction as a means to catch their prey and the unique defence of the hagfish has evolved to counter this means of attack. Almost a litre of slime is released but it contains only about 20 mg of filaments and 15 mg of mucins, and so is mostly water. The intermediate filaments have interesting mechanical properties due to their structure. They start as helically coiled α-keratins, like much of wool and hair intermediate filaments. When acting as structural members, in all biological cells as well as in hagfish slime, intermediate filaments are bundles of nanofibres suspended in liquid. As such they can be extended to large strains with little applied load, i.e. they are very soft. At larger strains, liquid is expelled, and then at even greater strains the α-keratins start to straighten into highly aligned β-sheets and become very stiff. High strength, high modulus spider silk is mostly β-sheets. For intermediate filaments within living cells, by the time this state is reached, the cell has deformed beyond survival but the intermediate filaments provide the strength to avoid complete tissue failure (Fudge *et al*., 2009).

2.6.6 Bacterial cellulose

The bacteria *Acetobacter xylinium* synthesises cellulose within its single cell to produce a long thread that protrudes from one end. The thread is highly crystalline, pure cellulose and has a diameter of a few tens of nanometres. Being a single crystal of cellulose, it has very high specific strength and, if they could be isolated and aligned, would produce a high-strength material. The bacteria live in large colonies and are quite easily cultured. The large cell culture forms a mat of fibres that can be harvested and the bacteria, which are killed, form only a small part of the mass of the fibre mat (Fig. 2.24). In some parts of the world, the gel of nanofibres is used as the base for a sweet dessert.

Tests have been made on individual fibres in three-point bending mode on suspended nanofibres using atomic force microscopy (Guhados, 2005). These gave a measurement for Young's modulus of 78 GPa, which is quite stiff. The fibres would also be expected to be very strong but could not be tested to failure with this method. According to Yano *et al*. (2005), the cellulose nanofibres have a density of 1.6 g/cm^3, modulus of 138 GPa, and tensile strength of at least 2 GPa (125 cN/tex), which is stronger than ballistic nylon. Despite these properties, however, bacterial cellulose



2.24 SEM of a bacterial cellulose sheet.

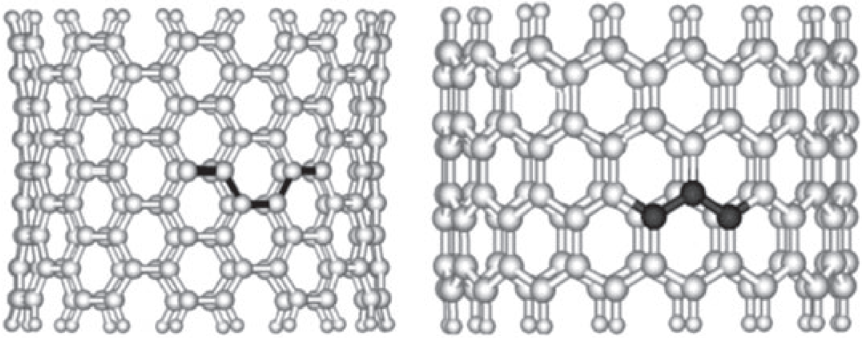
nanofibres have yet to be harvested in sufficient quantities to find commercial application. They continue to be studied and are of particular interest in the biomedical composites field because of their inherent biocompatibility.

2.7 Carbon nanotubes

2.7.1 Properties

Carbon nanotubes represent the strongest material known on earth; in addition, they have the highest thermal conductivity and are moderately electrically conductive. With these outstanding and potentially useful properties it is not surprising that a great deal of research effort has been expended in producing them, studying them, and trying to turn them into useful products. Unfortunately, it is fair to say that their initial outstanding promise has yet to be fulfilled and there may be fundamental reasons why this is so.

Carbon nanotubes can be considered as sheets of graphene rolled into tubes. In single-walled carbon nanotubes (SWCNT) they consist of a single sheet and in multi-walled nanotubes (MWCNT) many concentric tubes are nested together. The carbon atoms within a sheet are covalently bonded into hexagonal rings joined into a honeycomb structure. Each atom has three neighbours bonded to it by the sp2 covalent bond, which is extremely strong and stable. The ends may be closed into domed caps and the convex

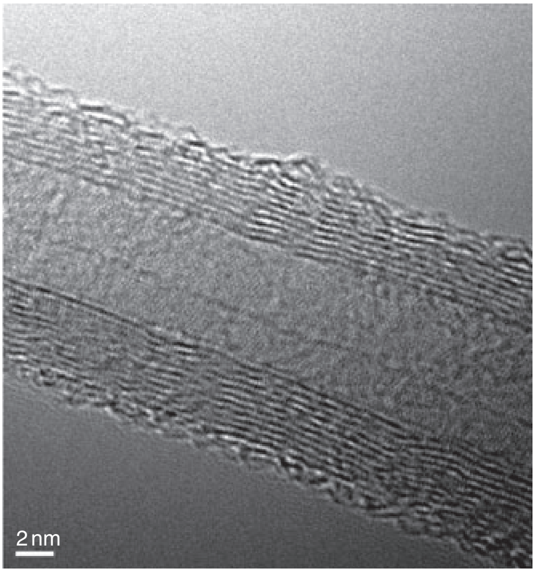


(a) (b)

2.25 Single-wall carbon nanotube structure. (a) Armchair structure, (b) zig-zag structure. (Adapted from Basiuk, 2002.)

curvature here is due to a switch to some pentagonal units in the structure. The curvature in the walls is due to rolling the flat sheet into a tube. There are a range of helix angles with respect to the hexagonal ordering through which a stable cylinder can be rolled. The limits of these are the 'armchair' and the 'zig-zag' shapes shown in Fig. 2.25a and b. The number of hexagonal units and the helix angle determine the diameter of the tubes or shells. Larger thin-walled tubes tend to collapse into ribbons with a dog-bone cross-section. While each individual carbon nanotube is very strong due to the covalent bonds between atoms, the interaction between tubes is much weaker as it is due to the Van der Waals interactions. The interaction between the concentric tubes within each MWCNT (Fig. 2.26) is also via Van der Waals only. Calculations suggest that the interaction transfers little stress between layers so that the outer shell carries almost all of an applied load.

The relatively low inter-shell, compared with intra-shell, bonding means that any applied load is predominantly carried by the shell to which it is applied, which usually means the outermost, rendering the other shells mostly redundant from a load-carrying perspective. However, the inner shells would resist compression of the outer shell and so add to stiffness and buckling resistance. The partially redundant shells of MWCNTs mean that single wall nanotubes show greater specific strength in comparison. Deformed MWCNTs, bent or compressed, might be expected to show better load sharing between the layers. The cause of the high individual nanotube strength is also one of the reasons that macroscopic assemblies of nanotubes are weaker than might be expected. The high individual strength is due to the perfect structure and the full occupation of all available carbon bonds. This means that nanotubes do not adhere well to other objects, such as composite resins, polymers, or to each other. The adhesion



2.26 Transmission electron microscopy (TEM) image of a multiwall carbon nanotube (MWCNT).

energy is due only to the dispersive component of the Van der Waals interaction, with no acid–base interactions and no covalent bonding to the polymer matrix. In order for a resin to form a chemical bond with the surface of the nanotube, a bond within the nanotube must be broken and so its inherent strength would be reduced. Functionalisation of the surfaces of nanotubes thus weakens them by breaking carbon–carbon bonds. Every strong chemical bond with a nanotube, even through addition of groups to provide acid–base interactions, must weaken it to some degree. A large number of bonds are required to effectively transfer stress from nanotube to nanotube so that they all take up the load simultaneously. A balance must be made between improvement to the interfacial shear strength and weakening of the tubes themselves.

Functionalisation can be achieved through aggressive chemicals such as fluorine or strong acid treatments, or through electron or ion bombardment. Chemical attack tends to form reactive groups at the caps and at defects on the sidewalls first and this, it could be argued, minimises the damage since the defects were already present and the caps contribute little to the nanotube's strength. With a few percent of the carbon atoms involved, an order of magnitude improvement in bonding can be achieved. Ion and electron treatments can form reactive surface groups or form cross-links between the layers of MWCNTs (Lordi and Yao, 2000).

When nanotubes interact directly with each other, this is also via the Van der Waals attraction, which is relatively weak and short range and so

Table 2.2 Properties of individual CNTs compared with other materials

	CNT	Steel	Carbon fibre	Copper	Graphite
Modulus (GPa)	~1000	210	~500–1000		
Tensile strength (GPa)	~20–100	~1.3	~3.5		
Density (kg/m^3)	~1330	~7800	~1750		
Thermal conductivity (W/mK)	~2000–6000	~60	2000 (axial)	~390	
Electrical resistivity (nΩ/m)	~340–1000	~170		~16	~3000–60 000

NB 1/nΩm = 10 MS/cm.

assemblies of pure nanotubes, without resin or other materials to bind them together, are also relatively weak. Cross-links can be formed but again, only at the expense of inherent CNT strength. For these reasons, the enormous strength of the individual CNTs is very hard to exploit on a macroscopic scale in assemblies of relatively short nanotubes. For maximum use of the inherent strength of nanotubes, the inter-nanotube adhesion must be maximised. For this to happen, they must either be bound together by a resin, be directly cross-linked to each other, or their Van der Waals interaction optimised by very high alignment, ordering, and close packing.

The properties of individual CNTs are compared to other materials Table 2.2.

2.7.2 Carbon nanotube composites

Apart from the scale difference, a carbon nanotube composite is very similar to any other fibre-reinforced composite and so may be expected to follow the composite 'rule of mixtures', which relates the modulus and strength of the composite to the properties and proportions of reinforcement fibre and matrix. Usually the fibre is very stiff and strong, and the matrix is a cured resin with lower modulus, lower strength, and higher extensibility. This allows the matrix to transfer stress between fibres so that each fibre takes up the load at the same time. In the absence of this stress transfer, each fibre may take the applied load sequentially, and when that load exceeds the individual fibre strength, that fibre breaks and load transfers rapidly to the next fibre and so on, such that the material fails at a much lower load than if all the fibres take the load at the same time. A form of the rule of mixtures is given by:

$$E_c = \eta_0 \eta_{LE} V_f E_f + (1 - V_f) E_m \qquad [2.5]$$

Here, E_c is the modulus of the composite, E_f and E_m are those of the fibre and matrix respectively, and V_f is fibre volume fraction. η_0 and η_{LE} are factors accounting for fibre orientation with respect to the load direction and fibre length, respectively. From Cox's shear-lag theory, an expression for η_{LE} can be derived:

$$\eta_{\mathrm{LE}} = 1 - \frac{\tanh(\beta L/2)}{\beta L/2} \qquad [2.6]$$

where

$$\beta = \frac{2}{d}\left[\frac{2G_m}{E_f \ln(R/r)}\right]^{1/2} \qquad [2.7]$$

and G_m is the matrix shear modulus, d is fibre diameter, R is fibre spacing and r is fibre diameter. A similar equation can be used for strength:

$$\sigma_c = \eta_0 \eta_{LS} V_f \sigma_f + (1 - V_f)\sigma_m \qquad [2.8]$$

Here σ_m is the stress in the matrix at the failure strain of the fibre, rather than the ultimate strength of the matrix, since the composite can be considered to have failed when the fibres break and this will occur at peak load if the fibres are stronger and stiffer than the matrix, as they have been designed to be. In this case, η_{LS} is the length factor derived from strength considerations rather than the modulus.

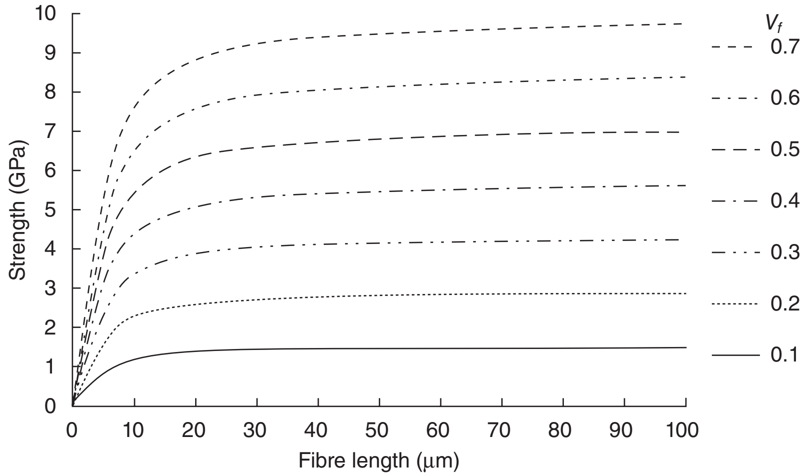
$$\eta_{LS} = (1/v_f)\left[\sum_i \frac{L_i v_i}{2L_c} + \sum_j v_j\left(1 - \frac{L_c}{2L_j}\right)\right] \qquad [2.9]$$

where L_c is the critical fibre length, derived by Kelly and Tyson (1965). Because the maximum load that can be applied to the fibre via the matrix depends on the area of adhesion of the fibre to the matrix, and hence on the length of the fibre and its diameter, the critical fibre length is the minimum length of fibre that can be exposed to the fibre breaking load via the matrix. Fibres shorter than the critical length would debond from the matrix before reaching the maximum stress they can sustain. Critical fibre length is given by:

$$L_c = \sigma_f d/2\tau \qquad [2.10]$$

where σ_f is fibre strength, d fibre diameter and τ is the matrix–fibre interfacial shear strength or the matrix shear strength, whichever is lower. In Eq. 2.9, v_i is the fibre volume fraction of fibres with length L_i where L_i is less than L_c and v_j is the volume fraction of fibres with length L_j, that is greater than L_c.

It can be seen from these equations that the adhesion between the fibre and the matrix, the fibre volume fraction, the fibre aspect ratio (L/d), and



2.27 MWCNT composite theoretical strength versus nanotube length for diameter of 10 nm, CNT strength of 20 GPa, IFSS of 20 MPa, and a range of fibre volume fractions. When the fibre or nanotube is longer than about ten times the critical fibre length (4.7 μm), about 95% of the maximum strength is achieved.

the fibre orientation distribution are key to the strength and modulus of the composite. There is no reason to suppose that this reasoning does not scale down to nanoscales. One difference may be that the Van der Waals forces may be less significant at macroscopic scales and more dominant at the nanoscale. If a carbon nanotube has a faultless surface of pure carbon, then the adhesion between it and any polymer matrix is only via dispersive (London's) Van der Waals interactions, but as the fibre diameter is so small in a nanotube this can still be quite high. Figure 2.27 shows the calculated dependence of composite strength (using Eqs 2.8 to 2.10) on fibre length for 10 nm diameter MWCNTs from 10 to 100 μm long with interfacial shear strength (IFSS) to the resin of 20 MPa and fibre volume fractions from 0.1 to 0.7. The Poisson ratio for CNTs and carbon fibres (~0.2) is much lower than for a typical matrix polymer (~0.3 to 0.4), and this means that under load the CNT resists compression and this may increase the interaction between them.

The critical fibre length equation can be re-written as the critical aspect ratio, $L_c/d = \sigma_f/2\tau$ which says that if the fibre is much stronger than the matrix, then the critical aspect ratio is very large. Put another way, if the fibre–matrix interaction is weak then the fibres have to be longer, but if they are very fine then they can be shorter. For SWCNTs the diameter is about 1.8 nm and so the critical fibre length is very short at 3.75 μm; however, SWCNTs are not readily available at these lengths and so are usually shorter than L_c which means that the full strength of the individual

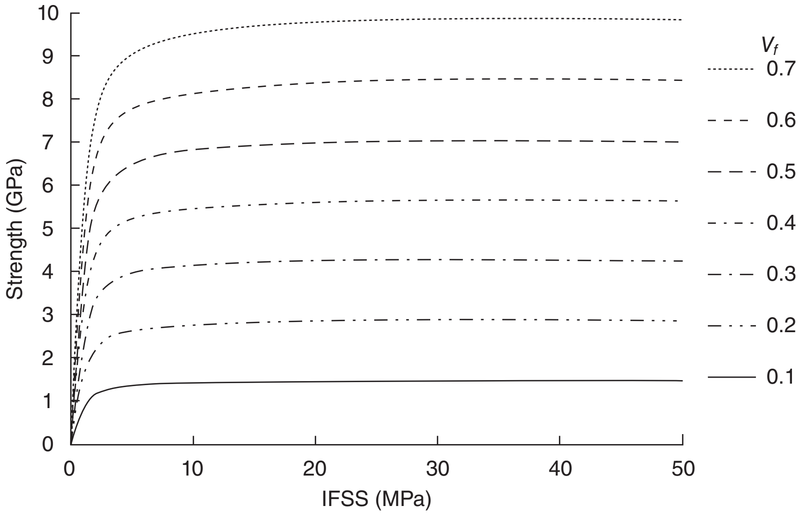
nanotubes cannot be realised. In addition, the short length, low aspect ratio, means that during drawing of the polymer–nanotube composite filaments, the nanotubes do not align as well with the filament axis as would be the case for higher aspect ratio nanofibres.

It is often assumed that the orientation efficiency factor for dispersed CNTs, η_0, has a value of around 0.2 for random dispersions and it has been found to be between 0.3 and 0.75 for drawn filaments or oriented films. In addition, the ends of short carbon fibres have been shown to localise stress when the composite is loaded. Stress localisation means that the stress is higher than the average near the localisation point. For instance, a hole drilled in a plate which is then placed under tension has the stress localised either side of the hole at 90° to the load direction, such that the local stress is up to an order of magnitude higher than the average and may exceed the material strength. Once a crack initiates, it can propagate because stress is localised at the crack tip and the whole material fails. In nanocomposites, there is the potential for stress localisation at the ends of the nanotubes and the shorter they are, the greater the number of ends, weakening the material.

Multiwall nanotubes of several mm in length can be made, but dispersing them in polymers is extremely difficult and the shear forces required to disperse them result in their breakage, drastically reducing the nanotube length. This, however, is not really the main issue for composites so long as the fibre length remains greater than about 10 critical lengths. The main issue is interfacial adhesion, which influences critical fibre length, and low fibre volume fraction. It can be seen from Fig. 2.28 that with 10 nm diameter MWCNTs of 100 μm length, the strength varies significantly as the IFSS increases and depends strongly on the volume fraction. The critical fibre length, the length required to apply a breaking stress to the fibre through the matrix, is longer the lower is the IFSS. The 100 μm nanotube length used in this example is less than L_c at the lowest IFSS and is about 12 times L_c at the highest IFSS. If the length is greater than this, then the length and the IFSS have little further influence and the composite fibre strength reaches its maximum.

It should be noted that the maximum possible volume fraction, even in theory, is that provided by hexagonal close packing of the fibres or tubes along their entire length. Since the nanotubes are finite in length and not perfectly oriented, they cannot be packed to a density even approaching this maximum. Some space is required between the fibres to allow a continuous volume of polymer to reside between them. This transfers the stress between fibres with lower cracking propensity than if the fibres were touching each other.

The closest packing densities and highest fibre volume fractions are achievable with continuous filaments, carefully arranged with no fibre



2.28 MWCNT composite theoretical strength versus interfacial shear strength (IFSS) for a range of fibre volume fractions from 0.1 to 0.7. Individual strength = 20 GPa, matrix strength = 100 MPa, diameter = 10 nm, and length = 100 μm.

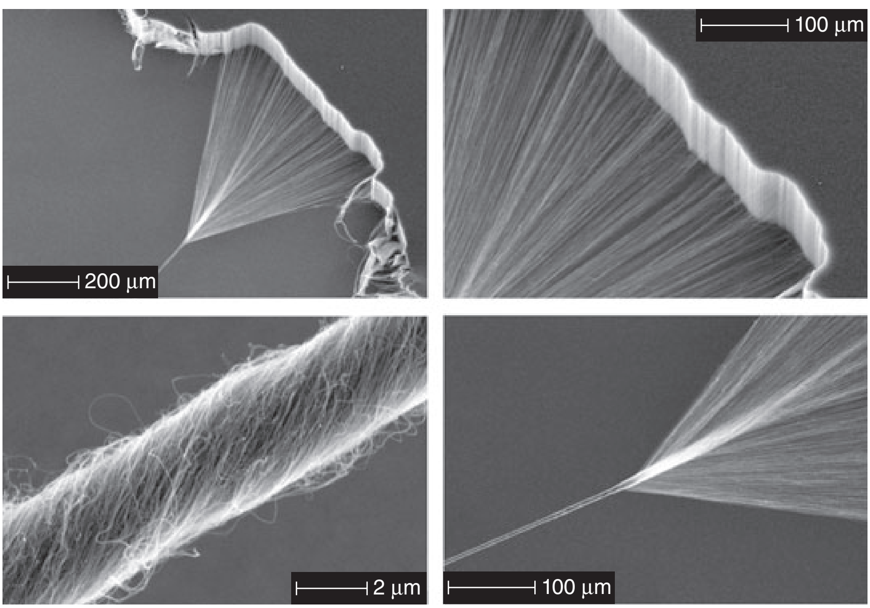
crimp. Composites made from these fibres are then extremely strong and stiff, but only in one direction. For strength in several directions, layers with different fibre orientations have to be built-up into multiaxial laminates. The directions are chosen to provide strength according to the loads that are expected in use. Currently, continuous nanotubes are not available, but they may be in the future and then their full strength may well be exploitable. At that stage, the strength may be limited by the frequency of faults.

When mixing nanotubes with polymers, the presence of the nanotubes greatly influences the polymer rheology. The viscosity of the mixture rises to unmanageable levels with high nanotube concentrations. If further dilution of the polymer with a solvent is impossible, as it is with melt spun polymers, then the viscosity cannot be controlled and stable fibre spinning is impossible. In coagulation spun nanocomposite fibres, fairly high volume fractions are possible with manageable viscosity, thanks to the high dilution of the polymer in a solvent. For instance, Young *et al.* (2010) achieved a fibre volume fraction of 26.5% with SWCNTs spun in Polyvinyl alcohol. The nanotubes had diameters of 1.8 nm and length 315 nm (0.315 μm), which is less than the critical fibre length. The variation in the strength of their fibres with diameter could be shown, using simple composites theory, to be due to a combination of volume fraction, nanotube orientation, and defect factors that, in turn, depended on the fibre diameter through the spinning process. However, the strongest specimen tested had a strength of

2.9 GPa (220 cN/tex) and modulus of 244 GPa (18600 cN/tex) but had low V_f at 2.2% and was not further drawn after spinning. Ko *et al.* (2007) electrospun MWCNTs in recombinant spider silk protein and achieved 4 GPa strength. Kumar *et al*. (2002) spun PBO fibres with SWCNTs and showed a 50% increase in strength but, while this was a significant improvement, it did not match the strength of commercial PBO fibres, which do not contain nanotubes. The improvement in strength of these already very strong materials is at least, in part, attributed to the improvement of alignment and crystallisation of the polymer molecules by the presence of the CNTs rather than by direct reinforcement of the polymer by them.

2.7.3 Dry spun carbon nanotube fibres and yarns

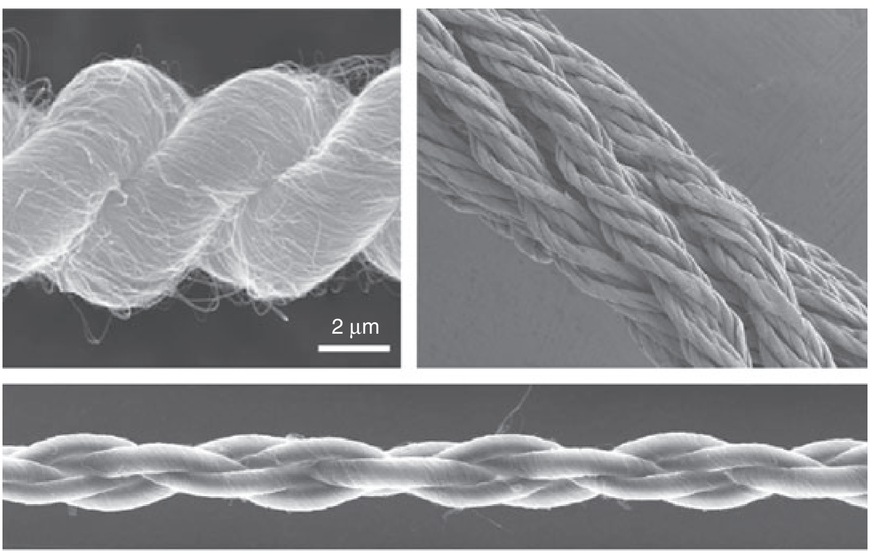
There are currently two methods of directly spinning dry CNTs: spinning webs drawn from a vertically aligned 'forest' of multiwall nanotubes (Zhang *et al*., 2004) and from an aerogel of double-walled nanotubes (Li *et al*., 2004). The first method is illustrated in Fig. 2.29 and uses a forest of MWCNTs that are grown on a silicon substrate. The wafer is coated with a thin layer of iron catalyst (~2.5 nm) on top of a thin silicon oxide layer (50 nm). The wafer is heated in a furnace in a controlled, flowing, atmosphere containing an inert gas and a hydrocarbon source such as acetylene. The iron layer



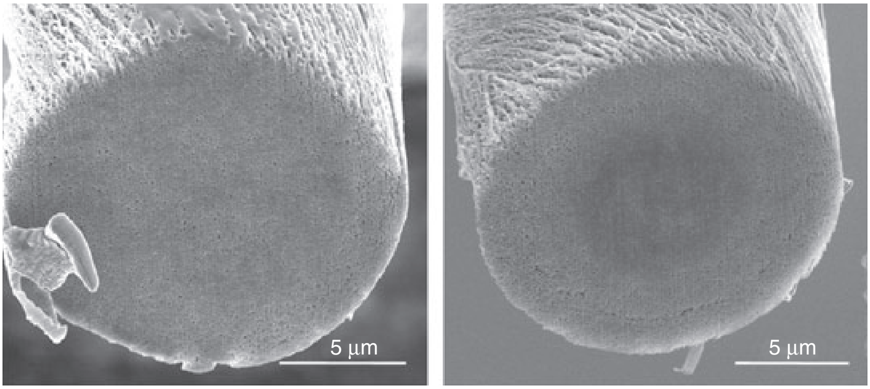
2.29 Direct spinning of MWCNTs from a vertically aligned nanotube forest.

breaks up into nano-sized catalyst particles adhered to the oxide surface layer and from which CNTs grow vertically from the base upwards. When the process conditions are just right, the density, purity, and degree of mechanical and Van der Waals interactions between the nanotubes allows them to be drawn off the substrate, parallel to its surface, into a web of partially aligned nanotube bundles. This web can then be condensed and twisted to form a yarn in a process very like conventional textile spinning, except that the number of 'fibres' in the yarn cross-section is much higher than in a conventional yarn. The condensed 'yarn' has the dimensions of a single polymer fibre (~10 μm), but has quite high porosity, with volume density of around 1.0 g/cm^3 compared to graphite density of ~1.8 g/cm^3. The yarn density can be further increased by wetting the web at the twist point with a volatile organic solvent so that, as it evaporates, capillary action pulls the nanotube bundles together. A wide variety of macroscopic structures, such as plies and braids, can be formed from nanotube yarns, as shown in Fig. 2.30.

In a conventional staple fibre yarn, the twist means that when the yarn is extended, radial pressure on the fibres increases inter-fibre friction and locks the fibres together. This means that the fibres share the applied load roughly simultaneously and equally, so that strength is maximised and from 60 to 90% of the individual fibre strength is expressed in the yarn strength. With CNT yarns, however, the strength achieved is less than 4% of the individual nanotube strength. Much effort has gone into understanding why



2.30 Various structures achievable using MWCNT dry spun yarns.



(a) (b)

2.31 FIB milled MWCNT yarn showing (a) the solid structure, twist = 15/mm, and (b) the sheath core structure developed by higher twist (25/mm). (Reprinted from *Carbon*, K. Sears *et al.*, 'Focused ion beam milling of carbon nanotube yarns to study the relationship between structure and strength', Vol. 48, pp. 4450–4456, Copyright 2010, with permission from Elsevier.)

this is so because exploitation of even 50% of the individual CNT strength would provide a new material that would outperform all current high-performance fibres.

Sears *et al.* (2010) used focussed ion-beam milling (FIB) of dry-spun MWCNT yarns within a scanning electron microscope to study the structure of spun yarns as a function of twist, and they related the findings to the tensile properties of the yarns. It was shown that the twist does not operate in the nanotube yarn as it does in a conventional yarn; the higher twist was detrimental to the yarn strength, as a sheath–core structure developed with a low-density sheath and a dense core (see Fig. 2.31). The excess twist separated the nanotube bundles so that they then could contribute little to the yarn strength.

The twisting seemed only to provide a mechanism to increase density and improve nanotube interactions. Untwisting of a nanotube yarn after the spinning operation has also produced no loss in strength, suggesting that radial pressure generation on axial loading was not the mechanism determining yarn strength, as it is in conventional twisted yarns.

As with polymer nanocomposite fibres, it is desirable for the load to be taken up equally by all the nanotubes simultaneously, otherwise they will break sequentially so that the whole structure eventually fails at low applied loads. The interaction between the nanotubes is via Van der Waals interactions (or 'static friction'). Within bundles the nanotubes are parallel, with their ends aligned, and closely packed so that the interaction within each bundle is strong and the bundles are relatively stiff. Between bundles there

is contact at only a few places and the interaction between bundles is fairly weak. It is not so weak, however, that a drawing operation could easily align them and improve their interaction. The stronger interaction between the nanotubes within each bundle, in which their ends are aligned, means that they cannot be easily made to overlap at the individual nanotube level, which is required for maximum load sharing.

To illustrate the concept, consider an extreme case of a hypothetical nanotube assembly (or a fibre assembly) built with bundles of tubes having their ends aligned and then the bundles joined end to end. Clearly, this would be a very weak structure, in contrast to one with uniformly overlapping, densely packed tubes. Bundles cannot be packed as closely as individual tubes and so also reduce the inter-nanotube adhesion, reducing strength. Various methods have been tried to allow drafting of the nanotube fibres to straighten, align, and overlap the nanotubes but none has so far succeeded, and so the strengths achieved have yet to surpass the best high-performance fibres already available. However, the high toughness, high thermal and electrical conductivity, and good biocompatibility, plus the potential for outstanding strength and stiffness, mean that interest in them has not waned.

The difficulties in dispersing nanotubes and then achieving high fibre fractions in nanocomposite fibres are partially ameliorated in dry spun fibres because the nanotubes are already closely packed and highly aligned. If infused with resin by capillary action, a high fibre volume fraction can be more easily achieved.

2.7.4 Direct yarn spinning from CNT aerogel

Windle's group at Cambridge University has developed a method of dry-spinning CNTs that has high potential for becoming a continuous process, more like conventional fibre extrusion (Li *et al.*, 2004). The CNTs are formed in a high temperature cylindrical furnace from a hydrocarbon gas in the presence of a catalyst. The nanotubes are mostly double walled and have large diameter so that they collapse into ribbon like nanotubes with dog-bone cross-section. These nanotubes have high specific strength and low redundancy of layers, and the potential for high inter-nanotube contact within the yarn structure. The presence of metal catalyst particles in quite high concentrations may be a problem for toxicity and raises concerns about their use in medical applications, as well as occupational health and safety issues in their handling. However, similar issues arise for most nanomaterials and will have to be overcome or they will not be adopted.

The aerogel process of producing carbon nanotube fibres would probably be the easiest to scale-up to commercial production since it already produces continuous lengths of material. The properties of any CNT fibre have

yet to surpass currently available polymer fibres in strength and modulus, and so the other unique properties of CNTs such as electrical and thermal conductivity and biocompatibility are likely to be exploited first, in combination with their good, but not exceptional, specific strength.

2.8 Conclusion and future trends

Further work will continue in developing high specific strength fibres, and probably nano-reinforcement or nano-fillers will play a part, even if only to enhance polymer molecular alignment and crystallisation of new polymer molecules. Carbon nanotubes of indefinite length will most likely become available and then their defects will be the limiting factor in their performance.

Electrospinning is becoming more widely exploited on an industrial scale and its use will increase as more products are seen in the market place and manufacturers perceive less risk in its adoption. The products most likely to benefit are filter media, barrier fabrics, and medical textiles, but nanofibre sensing textiles will also be developed. There is much opportunity for innovation in this field, with commercial bicomponent and multi polymer systems, perhaps including functional particles, expected to be the first to follow more conventional but large-scale electrospinning systems. The exploitation of natural nanofibres will probably be developed, either through their extraction from plants and animals or through recombinant technology. Recombinant technology, in which the genes for a particular protein are transplanted into and expressed by a bacteria, allows large-scale fermentation with high yield and good quality control. This reduces the variability and unreliability of natural systems.

There is a genuine need for protective clothing that does not cause physical, especially thermal, stress to the wearer and so lighter weight and more breathable fabrics are likely to be a key development requiring new or improved materials. Electronic textiles with actuation of pores are one such possibility. These would automatically close only when required, for instance when a chemical threat was sensed, and so would reduce the thermal stress of the wearer but allow them to wear the protective clothing all the time. Sensing and other electronic textiles suffer from the problem that the continuing miniaturisation of discrete devices starts to remove the need, and even the desirability, of having the electronics fully integrated into the textile, except perhaps for certain specialist areas such as military apparel.

There are difficulties with the laundering and durability of integrated electronics. Combined with the need for every fully integrated component to be included in every set of clothing, this means that the motives for fully integrating the electronics into the textile can sometimes seem rather contrived. For instance, personal communication devices are not washable and

expensive, and are currently wisely moved from one suit of clothing to the next. Their integration into a garment would require a new device for every jacket worn. It is more likely that generic flexible conductors, sensing and actuating fibres, and simple switches will continue to be fully integrated into protective clothing through weaving, embroidery, and computerised knitting and these will connect to discrete, intelligent, electronic devices that can be transferred from garment to garment.

2.9 References

Basiuk, VA (2002) Reactivity of Carboxylic Groups on Armchair and Zigzag Carbon Nanotube Tips: A Theoretical Study of Esterification with Methanol. *Nanoletters.* 2, 8: 835–839.

Bhat, NV, Seshadri, DT; Radhakrishnan, S (2004) Preparation, Characterization and Performance of Conductive Fabrics: Cotton + PANi. *Textile Res. J.* 74 (2): 155–166.

DiOrio, AM; Luo, X; Lee, KM; Mather, PT (2011) A Functionally Graded Shape Memory Polymer. *Soft Matter.* 7 (1): 68.

Downing, SW (1984). The Hagfish Slime Gland Thread Cell 1. A Unique Cellular System for the Study of Intermediate Filaments and Intermediate Filament–Microtubule Interactions. *J. Cell Biol.* 98: 653.

Fiberio (2011) http://www.fiberiotech.com/ [accessed 03/12/2011].

Fudge, DS *et al.* (2009) From Ultra-soft Slime to Hard a-Keratins: The Many Lives of Intermediate Filaments. *Integr. Comp. Biol.* 49 (1): 32–39.

Gregor-Svetec, D; Sluga, F (2005) High Modulus Polypropylene Fibers. I. Mechanical Properties. *J. App. Polym. Sci.* 98, 1.

Guhados, G; Wan, W; Hutter, JL (2005) Measurement of the Elastic Modulus of Single Bacterial Cellulose Fibers Using Atomic Force Microscopy. *Langmuir*. 21 (14): 6642–6646.

Hearle, JWS (2004). *High-performance Fibres*. Woodhead Publishing Ltd, Cambridge, UK and The Textile Institute. ISBN 1855735393.

Hills Inc. (2011); http://www.hillsinc.net/nanomeltblownfabric.shtml [accessed 29/11/2011].

Jones, L (1975). The Isolation and Characterization of α-Keratin Microfibrils. *Biochimica et Biophysica Acta.* 412 (91).

Kalder, K; Holmes, D; Trotter, J; Chapman, J (1996) Collagen Fibril Formation. *Biochem. J.* 316 (1).

Kelly A; Tyson, WR (1965) Tensile Properties of Fibre-reinforced Metals: Copper/tungsten and Copper/molybdenum. *J. Mech. Phys. Solids.* 13, 329.

Kitagawa T (1998) Morphological Study on PBO Fiber. *J. Polym. Sci., Polym. Phys.* 36: 39.

Ko FK; Sakigara, S; Gandhi, M; Ayutsede, J (2007) *Electrospun Carbon Nanotube Reinforced Silk Fibers.* USP 20070082197.

Kumar, S *et al.* (2002) Synthesis, Structure, and Properties of PBO/SWNT Composites. *Macromolecules*. 35: 9039–9043.

Lendlein, A; Jiang, HY; Junger, O; Langer R (2005) Light-induced Shape-memory Polymer. *Nature*. 434: 879–882.

Lendlein A Kelch S (2002) Shape-memory Polymers. *Angew. Chem. Int. Edn*. 41: 2034–57.

Li Y-L; Kinloch LA; Windle AH (2004) Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis. *Science*. 304: 276.

Lordi V, Yao N (2000) Molecular Mechanics of Binding in Carbon Nanotube–Polymer Composites. *J. Mater. Res.* 15 (12):2770–9.

Meng, Q; Hu, J; Zhu, Y; Lu, J; Liu, Y (2007) Morphology, Phase Separation, Thermaland Mechanical Property Differences of Shape Memory Fibres Prepared by Different Spinning Methods. *Smart Mater. Struct.* 16: 1192–1197.

Nakata, K; Fujii, K; Ohkoshi, Y; Gotoh, Y; Nagura, M; Macromol. (2007) Rapid Commun. 2007, 28, 792–795.

Russell, SJ (Ed) (2006), *Handbook of Nonwovens*, Woodhead Publishing, Cambridge, UK.

Sears, K; Skourtis, C; Atkinson, K; Finn, N; Humphries, W (2010) Focused Ion Beam Milling of Carbon Nanotube Yarns to Study the Relationship Between Structure and Strength. *Carbon*. 48 (15): 4450–4456.

Shima Seiki (2011) http://www.shimaseiki.com/ product/knit/

Sikkema DJ (2002). Man-made Fibers, One Hundred Years: Polymers and Polymer Design. *J Appl. Polym. Sci.* 83: 484–488.

Skotheim TA; Eisenbaumer RL; Reynolds JR (1998) *Handbook of Conducting Polymers*, Vol. 1 and 2, Marcel Dekker Inc., NewYork.

Stoll (2011) http://www.stoll.com/ [accessed October 2011].

Textile Glossary (2011) http://www.textileglossary.com/terms/smart-textiles.html [accessed March 3, 2011].

Textile School (2011); www.textileschool.com/school/weaving [accessed October 2011].

Vollbracht L; Veerman, TJ (1976) *US Patent 4308374*.

Volokhina, AV (2002) Effect of the Molecular Weight of Fibre Forming Polymers on the Mechanical Properties of Polymer Fibres. *Fibre Chem.* 34 (1): 3–11.

Xue, P; Tao, XM; Keith, WY; Kwok, MY; Leung MY; Yu, TX (2004) Electrochemical Behavior of Fibers Coated with an Electrically Conductive Polymer. *Text Res. J.* 74 (10): 929–936.

Yano, H; Sugiyama, J; Nakagaito, AN; Nogi, M; Matsuura, T; Hikita, M; Handa, K (2005) Review on Auxetic Materials. *Adv. Mater.* 17: 153.

Young, K; Blighe; FM; Vilatela; Juan J; Windle AH; Kinloch IA; Deng L; Young, RJ; Coleman JN (2010) Strong Dependence of Mechanical Properties on Fiber Diameter for Polymer Nanotube Composite Fibers: Differentiating Defects from Orientation Effects, *ACS Nano.* 4, 11: 6989–6997.

Zhang M; Atkinson KR; Baughman RH (2004) Multifunctional Carbon Nanotube Yarns by Downsizing: an Ancient Technology. *Science.* 306: 1358–61.

3
Smart surface treatments for textiles for protection

E. SHIM, North Carolina State University, USA

Abstract: Surface treatments are one of the most effective ways to impart functionality to textiles and fibers. The surface is where a material first responds to and interacts with the environment. Ideally, a smart protective surface will sense the environmental hazard – thermal, radiation, or chemical in nature – and respond to it to block it from harming the human body, while not interfering with moisture and air interchange through it to provide comfort. Various surface treatment methods have been introduced to impart smart, adaptive properties for protective systems. They include the polymer brush system, which has gained considerable interest as it can achieve drastic surface modifications through chain conformation changes, and coatings that can be utilized to create smart surfaces for protective clothing. This chapter also includes descriptions of other coating methods and smart materials such as phase-change polymers, shape-memory polymers, nanoparticles, and conductive materials that can be introduced to textile systems through coating technology. Other novel techniques, such as nanolayer deposition and nanofiber coating, are also briefly discussed.

Key words: surface treatments, polymer brushes, coating, smart materials.

3.1 Introduction: the role of surfaces in smart fabrics for protection

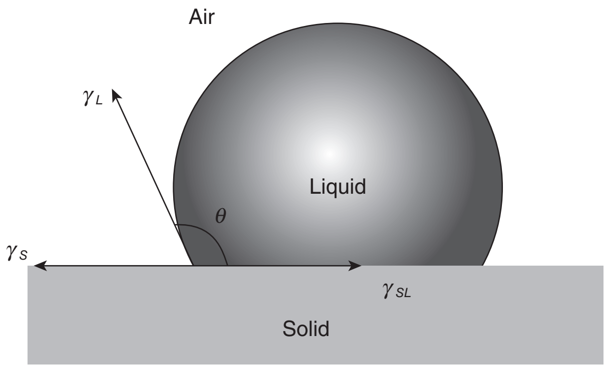
A surface is where a material encounters its environment and it determines how a material interacts with its surroundings. Many properties, such as adhesion, wettability, adsorption, charge dissipation, chemical affinity, friction, and barrier properties, are governed by surface characteristics. The contribution of surface properties can be more important in textile materials than others since they have large surface areas. Therefore, surface engineering of fibers and fabrics has been a subject of interest in the research and development of value-added and functional fabrics. The engineering and control of surface characteristics is of the utmost importance in many applications such as medical textiles, filtration, hygiene products, technical textiles, and apparel. In smart and protective fabrics, surface again plays an essential role in bringing the required functionality needed to an application.

Protective clothing is designed to protect the human body from external hazards. It forms a barrier against environmental threats, such as chemical, thermal, mechanical, biological and radiation hazards, while maintaining a safe and comfortable micro-climate around the skin (Raheel, 1994). Fabrics used for protective clothing should prevent penetration of unwanted compounds and energy, so it is important to maximize their barrier properties. At the same time, they should interfere minimally with the release of moisture from the human body and the passage of air, so fabrics have to be air and moisture permeable. The main challenges in developing protective clothing have been in achieving these two contradicting goals – maximum protection and comfort (Shishoo, 2002). This leads to the pursuit of selective permeability in which a fabric blocks and captures only harmful compounds whilst being permeable to all other substances. Selective barrier technology has been used commercially, and successfully delivers comfortable protective clothing in applications areas such as surgical gowns, military uniforms, and sportswear. However, challenges still remain in achieving maximum safety without a sacrifice in comfort. This leads to an interest in finding smart and adaptive protective solutions that turn regular fabrics into a barrier, only when needed in response to environmental stimuli.

There are diverse types of environmental threats and they can be in the form of liquid, gas or energy. The type and nature of any threats are determined by the application area, so protecting the human body requires an understanding of each threat it encounters during use. Generally, the properties required for high-performance protective clothing are barrier properties, permeability and selectivity. In addition a smart protective garment requires the ability to sense, respond and control. The contributions made by the surface characteristics to these properties are very critical.

One of the most fundamental requirements for protective clothing is the building of a barrier to liquid penetration; the reason is that liquids frequently are a carrier of harmful chemicals, viruses, or bacteria. Textile fabrics are porous media and liquids can easily penetrate through them. Penetration of liquid through a fabric occurs in two different ways: (i) fluid flow through the pore structure, and (ii) diffusion through the fabric itself. The former is mostly driven by wicking; that is, liquid uptake by capillary action, and the latter is mostly driven by diffusion of fluid molecules through fibers and other components. Thus, liquid penetration is the result of the combination of a variety of physical and chemical phenomena including wetting, wicking, and diffusion. Creating a liquid barrier requires the prevention of liquid penetration by blocking these pathways.

Repellency is one element that contributes to barrier performance. To provide a liquid barrier, the surface should be non-wettable. The most often used parameter describing the tendency of a liquid to wet or be repelled



3.1 Interfacial tensions and the static contact angle.

by the surface is the contact angle (Reynolds, 2005). Contact angle is defined as the angle between the liquid–air and solid–liquid interfaces when there is no relative movement of the contact line (Fig. 3.1). The static contact angle is determined by the balance of interfacial tensions in the three-phase contact line as described in Young's equation (Young, 1805).

$$\cos\theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \qquad [3.1]$$

where θ is the contact angle, γ_S, γ_{SL}, and γ_L are the interfacial tension between solid and air (solid surface tension), the interfacial tension between solid and liquid, and the interfacial tension between liquid and air (liquid surface tension), respectively.

The equation relates the static contact angle and interfacial tensions of liquid/air, solid/air and solid/liquid for conditions of thermodynamic equilibrium on a perfectly flat, homogeneous solid surface. A large contact angle indicates repellency: a liquid does not have the tendency to spread but forms droplets that can be easily removed from the surface. However, the surface of a textile substrate is not flat, but rough and porous, and the contact angle determined by the surface and interfacial energy through Young's equation cannot completely explain the wetting and repellency characteristics of such a surface. Since fabrics can be described as porous media, penetration through pores is often explained by capillary wicking. Capillary pressure is determined by the Young–Laplace equation (Adamson and Gast, 1997).

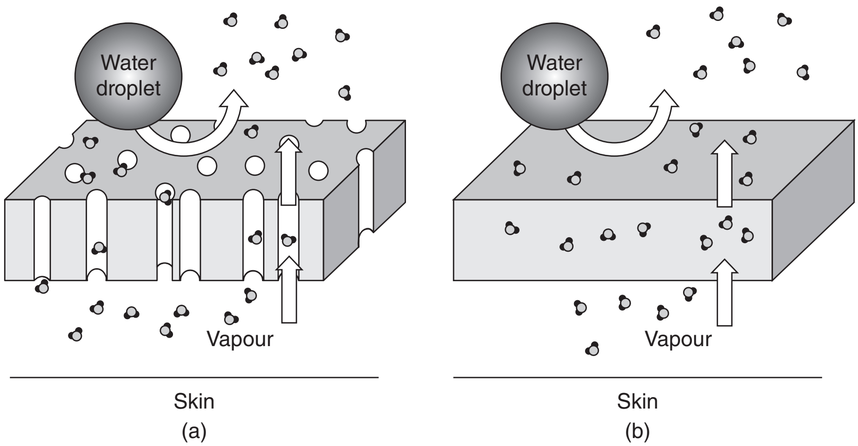
$$\Delta P = \frac{2\gamma\cos\theta}{r} \qquad [3.2]$$

where, ΔP is capillary pressure, γ is liquid surface tension, θ is contact angle, and r is the capillary radius.

Then, wicking is determined by pore geometry (pore radius, r) and surface chemistry (contact angle, θ) in a given fluid. The contact angle determines the direction of capillary pressure, and the tendency for liquid to penetrate through the pores. Wicking occurs only when the contact angle is less than 90°, which produces a positive capillary pressure. Then positive capillary pressure favors intrusion of liquid into pores, so a liquid spontaneously penetrates through the fabric. To prevent liquid from penetrating through pores, a high negative capillary pressure must be achieved and this can be accomplished by high contact angle. When the contact angle is greater than 90°, capillary pressure becomes negative and external force has to be applied to make liquid pass through the pores. The amount of pressure required for the liquid to penetrate can be described by Eq. 3.2. High contact angle and small pore radius are two critical components required for the creation of a liquid barrier. Contact angle is determined by surface chemistry and geometry, so surface treatment is a key to achieving surface repellency. Capillary radius, r, is affected by fiber size and fabric structure. So, fiber size, fabric openness, fabric construction, and any compression present during use affect the pore diameter and liquid penetration.

Thus, any surface treatment designed to improve liquid barrier properties is targeted to (i) increase contact angle and (ii) reduce pore size or eliminate pores altogether. In the history of fabric coating, protective rainwear was developed by coating a water impermeable film onto a fabric to provide water repellency (Kauffman and Seymour, 1990). One problem associated with this primitive protection technology is loss of comfort by drastically reducing the permeability to air and moisture.

To solve this problem, the second generation of protective clothing was designed to achieve a selective barrier property. This is the so-called 'breathable barrier' technology. A breathable barrier fabric is a selective barrier material that allows the dissipation of moisture vapor from the wearer while blocking penetration of liquid water or other liquids. It is a very effective way to achieve two of the most sought after attributes in protective garments – comfort and protection (Bitz, 2005). The most widely used technologies for producing breathable barrier fabrics involve either the use of a water-repellent treated, densely woven fabric, or a coating, or a laminated barrier film on a base fabric. Films can be either micro-porous or monolithic. Both a water-repellent, densely woven fabric and a microporous breathable film use a size exclusion mechanism to block the relatively large water droplets. The microporous breathable barrier film has micro-pores with controlled size and it blocks relatively large water droplets while permitting vapors to pass through the pore structures (Fig. 3.2a). The monolithic barrier film does not have any pores, so water droplets cannot penetrate. However, water vapor can permeate through the hydrophilic groups in the polymer structure–a process called 'active diffusion' (Fig. 3.2b) (Paul, 2009).



3.2 Selective permeability of breathable barrier. (a) Microporous film, (b) monolithic film.

Even though breathable barrier technology has been recognized as a breakthrough technology for protection, continuous efforts are being made to find better ways of achieving maximum protection without sacrificing comfort. There is a need for protection from a wide range of hazards, and these hazards may not be present all of the time, but only for an occasional exposure. In this case, fabrics with 'on demand' protection properties would be an ideal solution. Thus, 'a smart and adaptive approach' for the development of protection fabrics is a promising way to achieve this aim. One can imagine that the ideal protective clothing would have barrier functionality that is only activated when needed on sensing the hazard in the environment while the clothing retains its key components of comfort, i.e. no blocking of air and moisture transfer.

A smart material is a term describing a material that senses and reacts to environmental conditions. It is often called an intelligent, interactive or adaptive material (Meinander, 2005). Smart materials can sense, react and/or adapt to environmental stimuli. When they are exposed to the environment, first they sense the stimuli and process the signal, and then a reaction occurs. The stimuli can be force, temperature, radiation, chemicals, electric and magnetic fields, and responses can be movement, and changes in composition, shape, structures or properties (Tao, 2001; Meinander, 2005). To be a smart material, it should consist of components that sense, actuate and control. Smart textiles can be made directly from smart materials having all these functionalities or can be built as a system containing different components – i.e. sensors are embedded in the textile structure and communicate through conductive material to a controlling device and an actuator (Meinander, 2005).

As the surface is where a material is first exposed to the environment, surface functionality to sense and adapt as a response to environmental stimuli is one key component of a smart protective system. Various surface treatments have been demonstrated that have the ability to impart these surface functionalities. Different techniques and methodologies can be employed to render surface reactive properties. Photo-sensitive materials, conductive coatings, thermally sensitive materials, shape-memory materials, intelligent coating/membranes, chemically responsive polymers, mechanically responsive materials, microcapsules and micro and nanomaterials are a few examples of smart materials. These can be introduced through surface treatments on fabrics to create smart and adaptive surfaces (Tao, 2001; Haufe *et al*., 2005). The most common and well established techniques for surface functionalizations are grafting and coating. However, other novel techniques, such as nanolayer deposition and nanofiber coating, have been recognized as potential tools to create smart functional surfaces.

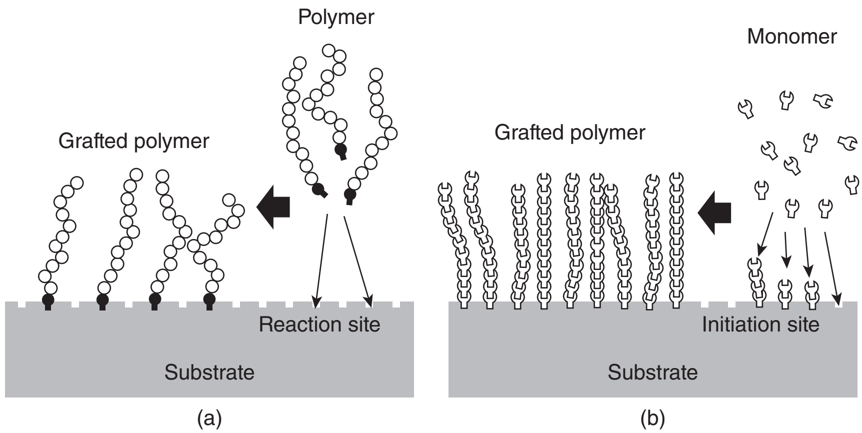
3.2 Surface grafting

3.2.1 The basics of surface grafting

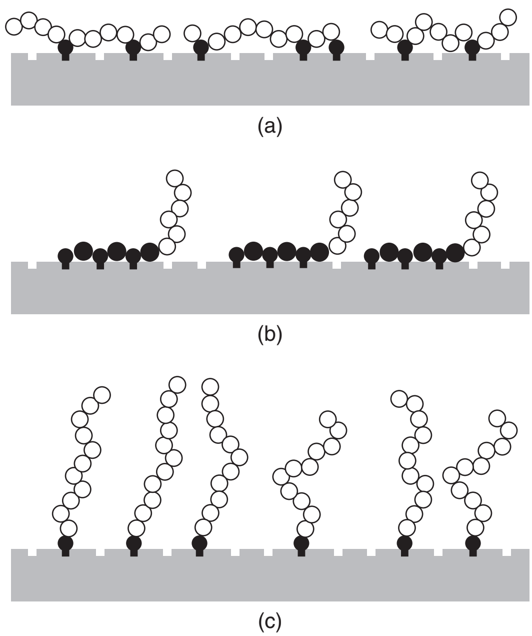
Grafting is one of the well-known methods to modify and functionalize polymer and fiber surfaces. Through a graft reaction, a second polymer is attached to the polymer backbone of the substrate with strong covalent bonds and, as the result, these 'grafted polymers' exhibit properties that are different from those of the original backbone. Especially, when dense polymer branches are produced on a fiber/polymer surface, its surface properties can be drastically changed. Surface dominated properties such as wettability, adhesion, and friction can be controlled by surface grafting of polymers.

There are two different routes to create surface grafting. These are called 'grafting-to' and 'grafting-from' techniques (Fig. 3.3) (Dyer, 2006; Park *et al*., 2010). In the 'grafting-to' method, preformed polymer chains are grafted onto the surface of the substrate polymer. Reactive parts of polymer chains (such as functional groups, radicals, etc.) react with substrate polymers and grafted branches are formed on the surface (Fig. 3.3a). The position and number of reaction sites in preformed polymers will affect the structure and thickness of the grafted polymer layer on the surface.

Grafting modes can be categorized into random side grafting, block side grafting, and end grafting, as illustrated in Fig. 3.4 (Park *et al*., 2010). Random side grafting occurs for a polymer with randomly distributed reaction units (Fig. 3.4a). A block copolymer with only one reactive block forms block side grafting where reactive blocks bond to the surface and are aligned parallel to the surface while the non-reactive blocks are freely stretched out



3.3 Schematics of surface grafting reactions for (a) grafting-to method and (b) grafting-from method.



3.4 Different grafting modes produced by the grafting-to technique: (a) random side grafting, (b) block side grafting, (c) end grafting.

from the surface (Fig. 3.4b) (Park *et al*., 2010). For polymers having a reactive group at only one chain end, only one end of the polymer chain is reacted and bonded to the surface (Fig. 3.4c). Therefore, end grafted polymers can freely change their conformation while their ends are anchored to the surface. However, this method produces only low to medium grafting density because a polymer chain has limited accessibility to an already grafted surface. When a surface is populated with grafted branches, a strong kinetic hindrance against grafting an additional polymer is present and inhibits further reaction (Tsujii *et al*., 2006).

In the 'grafting-from' method, monomers that can react onto the surface of the substrate polymer with the necessary catalyst are added, and polymer chains are directly grown from the substrate surface (Fig. 3.3b). This is also called 'surface initiated polymerization' (SIP). The reaction can be initiated chemically by using initiators such as a redox-initiator, or a photo-initiator. Plasma, glow discharge treatment, UV irradiation, electrobeam irradiation, γ-ray irradiation, or ozone treatment can also initiate the grafting reaction by producing active species (Xu, 2009). In both cases, free-radicals are created on the substrate polymer backbone and polymerization starts as monomers are added onto this site. As the reaction proceeds, the degree of polymerization, or chain length, increases. If there are two or more types of monomer, graft-copolymerization occurs and different surface properties can be engineered by controlling their ratio (Singh and Desai, 2004). In contrast to the grafting-to method, reaction is not hindered by already grafted polymer chains. To produce high-density grafted chains on a surface, the grafting-from method is preferred. Further discussion related to high-density polymer brushes on the surface achieved through the grafting-from method, and structure and properties created by it, are given in the next section (Edmondson *et al*., 2004; Tsujii *et al*., 2006).

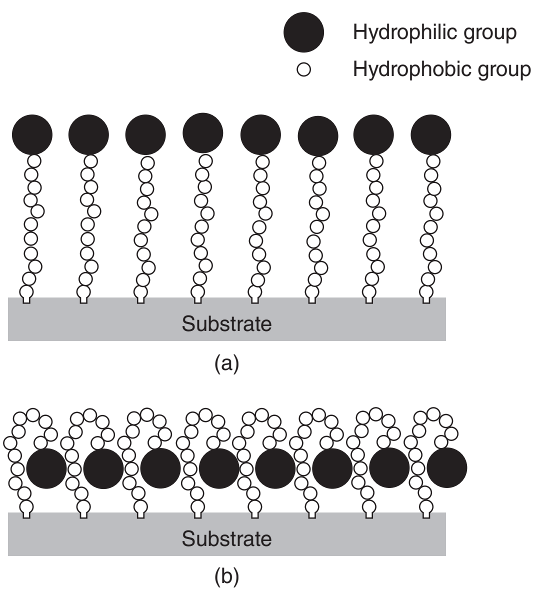
3.2.2 Reactive polymer brushes

In the case of end grafting, polymer chains are confined to the surface only by one end of the polymer chain, so they can realign and change chain conformation. When the graft density is low, they form a mushroom-like random coil conformation that is similar to the conformation of free chains, even though one end is confined by the substrate surface (Tsujii *et al*., 2006; Park *et al*., 2010). When the graft density of the polymer molecules becomes high, chains cannot form random coil conformations any more but form extended conformations where chains are aligned in the direction more or less normal to the surface, as shown in Fig. 3.3. This high density extended chain polymeric layer on the surface is called a 'polymer brush' (Mendes 2008; Milner 1991; Tsujii *et al*., 2006; Advincula, 2004). In contrast to other grafted polymers anchored in multiple points or a block, the high-density,

end-grafted polymer chains, i.e. polymer brushes, can form thicker layers and the thickness is directly related to the degree of polymerization of the brush chain (Park *et al.*, 2010; Tsujii *et al.*, 2006).

Polymer brushes can be anchored to the surface by physical absorption, but grafting forms durable polymer brushes through the formation of strong covalent bonds. Semi-dilute polymer brushes can be produced either via the grafting-to or grafting-from method, but high-density polymer brushes can be formed only with the grafting-from method (Park *et al.*, 2010).

Polymer brushes with their free end extended from the surface can undergo conformational changes as they are exposed to different environments (Sundaram *et al.*, 2003). As illustrated in Fig. 3.5, one end of the polymer brush is anchored to the surface, but chain conformation can change drastically, depending on the surrounding conditions, to minimize their free energy. They can be fully stretched, collapsed or bent. Frequently, conformational changes of a polymer chain lead to a significant change in the composition of the top surface and the resulting properties (Merlitz *et al.*, 2009). These changes can be reversible. Various environmental stimuli – light, solvent, temperature, pH, pressure, presence of ions and other compounds – can induce conformational changes of polymer brushes. Surface-dominated properties such as wettability, surface polarity, adhesion, biocompatibility, and adsorption are determined by the preferred brush

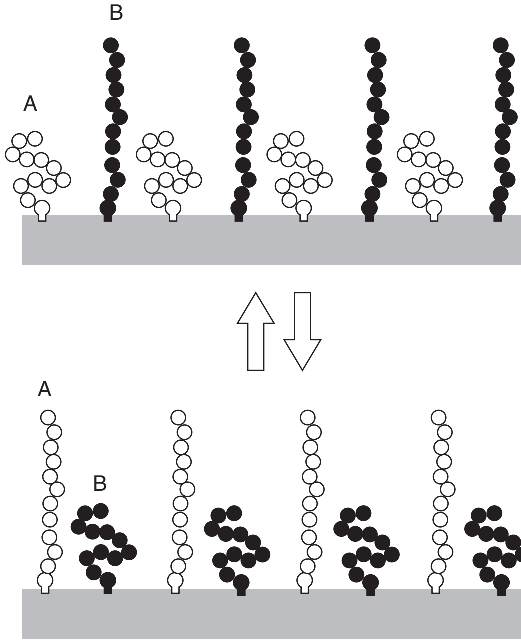


3.5 Alteration of surface properties by polymer brush chain conformation change. (a) Hydrophilic surface, (b) hydrophobic surface.

conformation, depending on the environment to which it is exposed (Russell, 2002; Luzinov *et al*., 2004; Kumar *et al*., 2008).

End-grafted polymer brushes can create a smart surface that interacts with the environment and switches its properties through reversible conformational changes in response to the environmental stimuli to which it is exposed. For example, polymer branches consisting of hydrocarbon chains and hydrophilic head groups can easily switch surface polarity according to solvents which they contact (Fig. 3.5). When these branches are stretched out from the surface, the surface becomes highly hydrophilic as hydrophilic groups dominate the surface (Fig. 3.5a). However, when it is exposed to the different conditions – such as solvent or ionic compounds, the hydrophilic head groups are pushed inside and the outermost surface layers become composed of non-polar hydrocarbons (Fig. 3.5b): the surface becomes hydrophobic (Fidalgo *et al*., 2009; Sundaram *et al*., 2003). As mentioned previously, environmental stimuli are not limited to chemicals or solvents. Sundaram *et al*., (2003) reported conformational transition by electrical potential. Photo-controlled surfaces produced by light induced conformational changes are also reported in the literature (Sundaram *et al*., 2003; Mendes, 2008; Zhang and Han, 2010). For example, photo-responsive molecules, such as spiropyran, undergo cis–trans isomerism depending on the wavelength of light to which they are exposed. Under UV light, the surface becomes hydrophilic with zwitterionic merocyanine conformation, while under the normal visible light it forms a hydrophobic conformation (Mendes, 2008; Higuchi *et al*., 2004; Edahiro *et al*., 2005).

Another interesting surface can be created by the use of mixed polymer brushes or block copolymer brushes (Zhao and Brittain, 2000; Kim *et al*., 2002). In the mixed polymer brush system, a surface is populated with two or more types of brushes which are incompatible with each other. Each type of polymer brush can react differently to environmental stimuli. Therefore, under one condition, the surface can be enriched by one brush (A) while the other brush (B) is collapsed (Fig. 3.6). Surface properties would be dominated by active brush A, while collapsed brush B would not affect surface properties. When environment changes occur which favor the second brush (B), surface properties are switched because the extended brush B dominates the surface properties while first brush (A) is collapsed (Fig. 3.6). Kumar *et al*. (2008) have reported on the surface properties of a mixed brush system of polystyrene (PS) and poly(2-vinylpyridine)(P2VP). A surface grafted with these mixed brushes becomes highly hydrophilic when treated with acidic water while toluene treatment makes it hydrophobic. This is because conformation changes of the brushes are caused by solvents with different polarity. P2VP chains are extended under acidic water while PS chains are collapsed and this conformation creates a more hydrophilic P2VP enriched surface. However when the surface is exposed



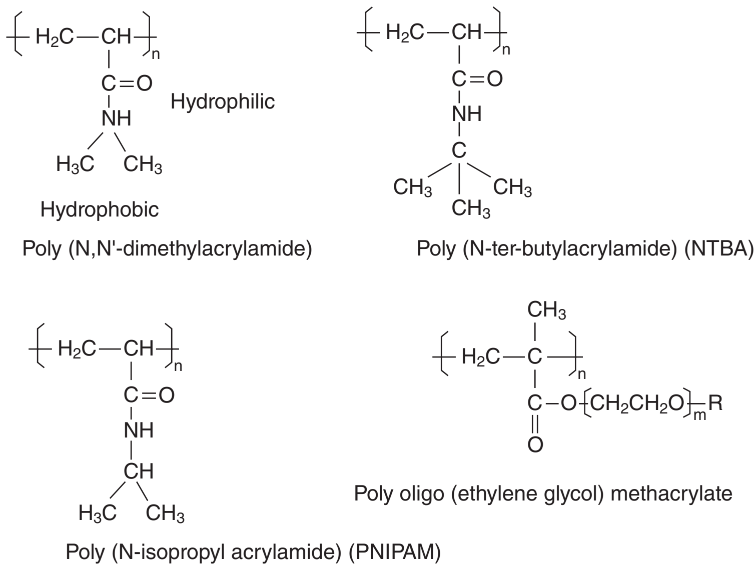
3.6 Possible conformations in mixed polymer brush system. For explanation see text.

to a non-polar solvent such as toluene, conformation is reversed. Now the surface is more or less like a PS monobrush surface and becomes hydrophobic (Kumar *et al.*, 2008).

3.2.3 Surface grafting of hydrogels

Another interesting material receiving considerable attention for smart textile application is a hydrogel (Carrillo *et al.*, 2008; Chen *et al.*, 2002; Liu *et al.*, 2009a). A hydrogel is a cross-linked hydrophilic polymer that can swell drastically and hold a large amount water (Sun *et al.*, 2004; Sen, 2008). Some hydrogels undergo changes in their volume and properties in response to environmental stimuli such as pH, temperature, ionic strength, solvent type, light, electric and magnetic fields, and the presence of chelating compounds (Carrillo *et al.*, 2008; Kopeček, 2007). A hydrogel can be either coated or grafted to the surface. Grafting results in a thin conformal layer on the fiber surface without blocking fabric pores, while fabric coating may cause significant changes in the pore structures of the fabric.

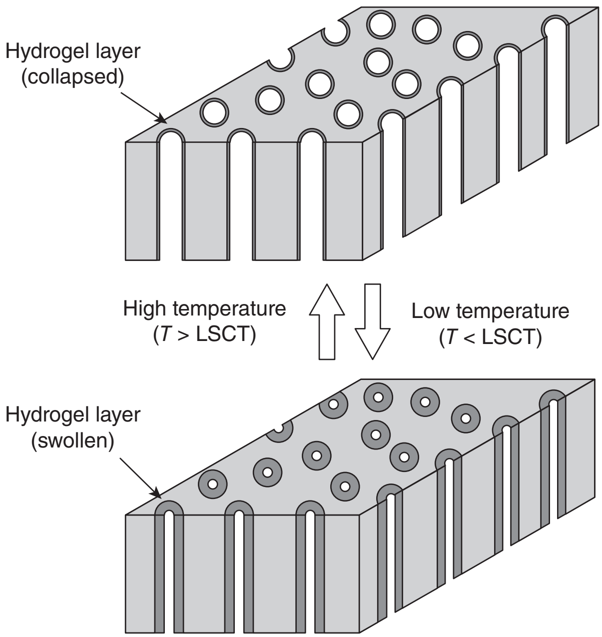
Hydrogels are polymers consisting of hydrophilic and hydrophobic moieties. Examples are poly (NN′-dimethylacrylamide), poly(N-ter-butylacrylamide)(NTBA), and poly(NN′-isopropyl acrylamide) (PNIPAM) (Fig. 3.7) (Jassal and Agrawal, 2010). They exhibit a reversible transformation from



3.7 Examples of hydrogel structures.

hydrophobic to hydrophilic form in response to temperature changes (Kopeček, 2007; Ryan *et al.*, 2005; Jassal and Agrawal, 2010). The transition temperature is called the 'lower critical solution temperature' (LCST) (Jassal and Agrawal, 2010). Below the LCST, chains are extended and absorb solvent by forming hydrogen bonds and they swell. Above the LCST, hydrogen bonds between the solvent and polymer become weak and chains collapse to a coil form with intramolecular hydrogen bonds and solvent is excluded. In this conformation, materials exhibit small volume and hydrophobic properties dominate. LCST can be adjusted by additives, or by modifying monomer structure or copolymer structures (Sen, 2008; Mendes, 2008; Sun *et al.*, 2004; Lin *et al.*, 1999; Carrillo *et al.*, 2008). Another category of thermo-responsive hydrogels is poly-oligo(ethylene glycol) methacrylates (POEGMA)(Fig. 3.7) (Lutz *et al.*, 2006). These can be made into various structures via controlled free radical polymerization techniques (Yamanaka *et al.*, 2011). They can be biodegradable and have advantages over the PNIPAM, including biocompatibility and resistance to absorption of proteins. They also can be used as building blocks for photonic hydrogels.

The volume and property changes of these materials caused by environmental stimuli can be used in various applications in protective clothing. One of the most promising applications would be a breathable barrier. A hydrogel layer grafted on pores of a microporous breathable barrier can swell or collapse in response to stimuli, and result in pore size changes (Fig. 3.8). For a thermo responsive hydrogel, at low temperature (below LSCT),



3.8 Hydrogel-coated microporous breathable barriers and their pore structures under different conditions.

hydrogel layers swell and the size of pores are reduced or blocked by swelling. Under this condition, permeability decreases and, in turn, evaporation and heat loss through the pores are reduced. At high temperature, the polymer chains are collapsed and the pores are opened up. Then, moisture can be easily released, helping evaporation of moisture from the human body and the release of heat, thus providing a comfortable environment under hot conditions (Jassal and Agrawal, 2010). Changes of moisture vapor permeability are not just the result of pore structure changes. Since swelling is caused by molecular chain conformation inside the gel, permeability through the gel is also altered, depending on the environmental conditions. Some changes of moisture vapor transfer rate (MVTR) as a function of temperature in these materials have been reported (Dyer, 2006; Ding *et al.*, 2006). Hydrogels can be responsive to other stimuli, such as light and solution pH (He *et al.*, 2009; Tao, 2001).

3.3 Coating techniques

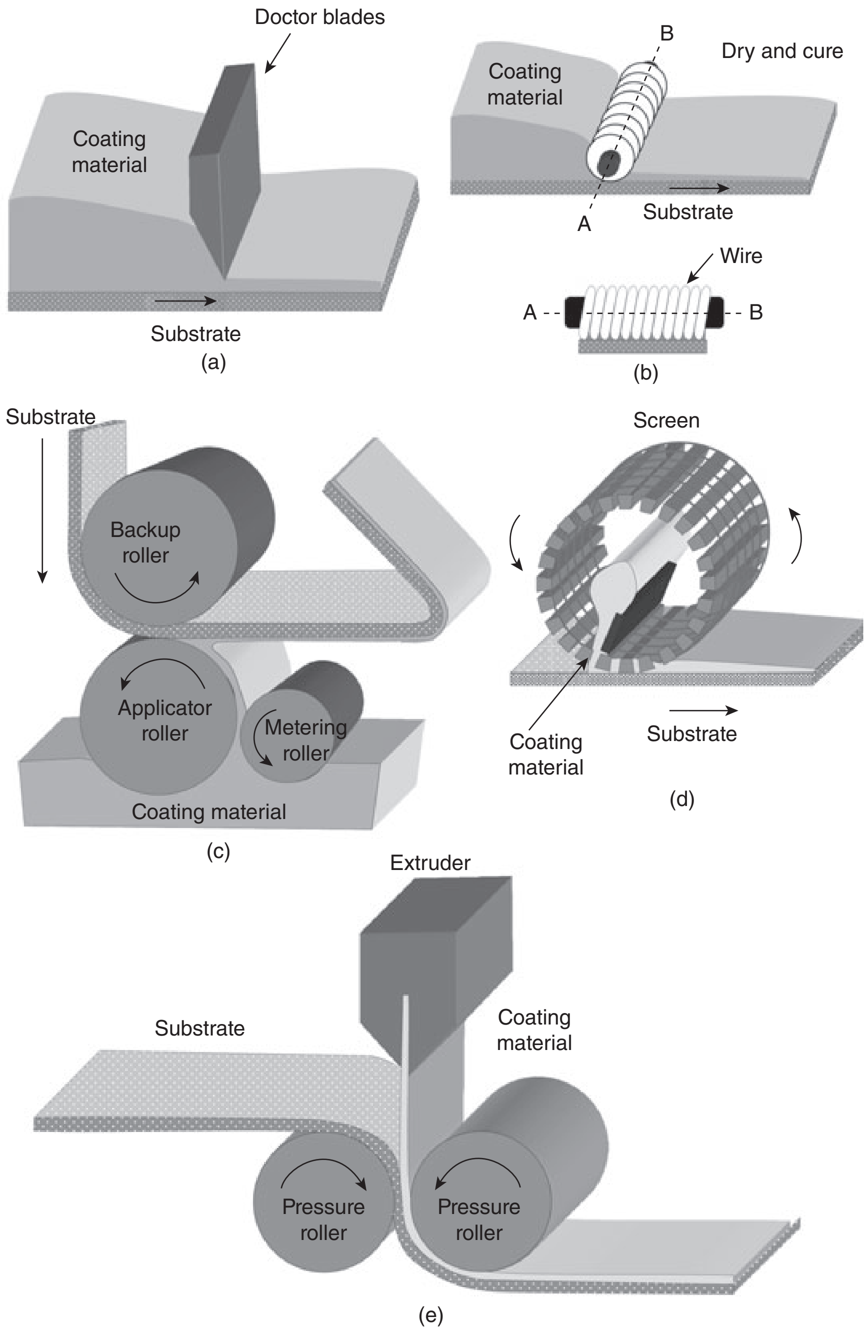
3.3.1 Principles and processes of textile coating

Coating is a process designed to deposit a layer of material on the surface of a substrate. Most conventional textile coating materials are fluids or

precursors of fluids (i.e. solid powders), and both film formation of coating materials and bonding to the substrate are required to achieve a quality coating. The coating process can be seen as a three-step process: 'metering, transferring and fixing' (Greer and Stelling, 1994; Scott, 1995). Metering controls the amount of coating material to be applied to the substrate, and it can be achieved using various metering devices – a displacement pump and a metering roll, or a metering knife or wire. In the transferring process, the coating material is deposited on the substrate and forms a coating layer. Various means are used to transfer coating materials to the substrate and these include a series of rollers or calendars, spray, direct extrusion to the substrate, or immersion of the substrate in a coating bath. To achieve a high quality coating, a uniform coating layer transferred onto the substrate with controlled penetration is desirable. The formation and penetration of coating layers on the substrate are affected by wettability, the rheology of the coating liquid, and the coating application technique used. Typically, the final step of the coating process is fixing, where the transferred and metered coating layers are fixed to the substrate through drying, curing or solidification. In this step, proper adhesion between the coating layer and substrate has to be achieved. A liquid film on the substrate becomes a solid coating layer and evaporation of the media or cooling down of the melt occurs. Polymerization reaction of polymer precursors and crosslinking reactions also occur during this step (Shim, 2010a).

A variety of coating techniques have been developed to accommodate wide ranges of coating materials and substrates, and some of these coating techniques are shown in Fig. 3.9 (Shim, 2010a). The simplest coating technique is immersion or saturation coating, where the fabric substrate is immersed in a bath of coating liquid to pick up the coating material. In this method, the amount of coating material applied is not metered, but is controlled by hydrodynamics and solution rheology. Most other coating methods use metering devices to control coating thickness.

Knife coating uses a metering blade to control coating thickness. In this process, the coating material is applied to the substrate and excess is removed by a metering blade. *Metering rod coating* is similar to knife coating but a metering rod (also called an applicator rod, a Mayer bar, an equalizer bar, a coating rod, or a doctor rod) is used to control the amount of coating material applied. *Roll coating* is a pre-metered coating technique and uses a series of rollers to meter and apply the coating material to a substrate. In this technique, the amount of coating material delivered to the substrate is nearly independent of the substrate structure since a film is metered and formed on the roller surface before it is applied to the substrate. Roll coating utilizes different numbers of rolls and types of rolls. Typically, one to four rolls are used in various configurations. When engraved rolls are used instead of flat rolls, liquid fills the engraving as the roll



3.9 Schematics of various coating methods. (a) Knife coating, (b) metering wire coating, (c) three-roll coating (L-head coating), (d) rotary screen coating, (e) extrusion coating.

rotates through the coating reserve, so the engraved patterns determines the amount of coating delivered. This process is called *engraved roll coating* (Hewson *et al.*, 2006; Grant, 1981). *Screen coating* is a process where coating materials are applied to the substrate through a mesh screen by a squeezing motion (Licari, 2003). Screen mesh number, squeeze pressure, the angle between the squeeze blade and the screen, and the rheology of the coating liquid affect the amount of coating material applied (Goossens, 2001). This is a good technique for lightweight and delicate substrates because little or no friction or tension is imposed on the substrate (Goossens, 2001). Another coating technique suitable for light weight fabrics is *transfer coating*. This is a two-step process where the coating material is first applied to a silicone release paper through one or other of the direct coating methods and then later transfers to the fabric substrate (Scott, 1995; Fung, 2002). It is more expensive than direct coating methods, but it can process lightweight fabrics and produce a flexible coated fabric because the process imposes little or no tension and yields low penetration (Fung, 2002; Keeley, 1991).

Spray coating is where a coating material is sprayed directly onto the substrate surface. There are various spray generation techniques such as compressed air vaporization, airless pressure spray, hot flame spray, hot vapor impelled spray, electrostatic spray, and dry powder resin spray (Licari, 2003; Waelde, 2001). Among them, the most common spray generation method is compressed air vaporization, where air and coating materials are passed out through a nozzle (Glawe *et al.*, 2003). In *slot die coating*, a coating material is pressed through a die and transferred directly on the surface of the fabric (Whiteman, 1993; Zickler, 1978). A traditional slot die configuration is a closed system where the die tip is in contact with the substrate and the coating material is not exposed to air during the process (Glawe *et al.*, 2003). In *extrusion coating* (Fig. 3.9c), molten polymer is extruded by an extruder pump through a die and deposited on the substrate. In most systems, there is a gap between the die tip and the substrate, where the extruded polymers are self-supporting. Adhesion can be improved by passing the deposited coating layer and the substrate through a pressure nip roller. *Scattered coating* is a method using solid powder, without a liquid medium, as a coating material (Waelde, 2001). In this process, coating powders are spread evenly on the substrate surface with a rotating scatter roller. The dosing roller, its rotation speed and the substrate line speed controls the deposition of coating powder on the substrate fabric (Jarrell, 1992; Glawe *et al.*, 2003).

The coating process can be very versatile and it can handle many different types of coating material through diverse processes and process controls. Through the coating process, a wide variety of smart materials, such as phase-change materials, shape-memory polymers and reactive hydrogels can be incorporated onto fiber and fabric surfaces. Another advantage of

the coating process in producing smart protective fabrics is its ability to apply multiple components without additional steps. One can carefully design coating formulations that are mixtures of different smart materials which can be applied to the substrate in one coating process step. Therefore, the coating process has the ability to deliver multiple functionalities.

Proper coating methods have to be selected depending on substrate and coating material characteristics, as well as the required layer thickness and penetration. The choice of coating process and material characteristics determines the amount of coating material applied to the substrate, uniformity of the coating layer, adhesion between the coating layer and the substrate, and the penetration of the coating material into the substrate (Scott, 1995). Thus, the performance and quality of a coated fabric requires an understanding of coating materials and the proper selection and control of the coating process. In the remaining part of this section, coatings of different types of smart materials will be discussed.

3.3.2 Superhydrophobic coatings

One of the basic elements of protective clothing is resistance to the permeation of fluids. A hydrophobic surface which has high contact angle and fluid repellency is essential in producing a fluid barrier. Water repellency coating in textiles is nothing new as the modern coating industry started with a rubber-coated waterproof garment (Kauffman and Seymour, 1990). Water repellent coated fabrics can be considered as the first protective cloth and it is still an important part of textile surface modification because its application has widened to include rainwear, upholstery, protective clothing and sportswear (Ramaratnam *et al.*, 2008).

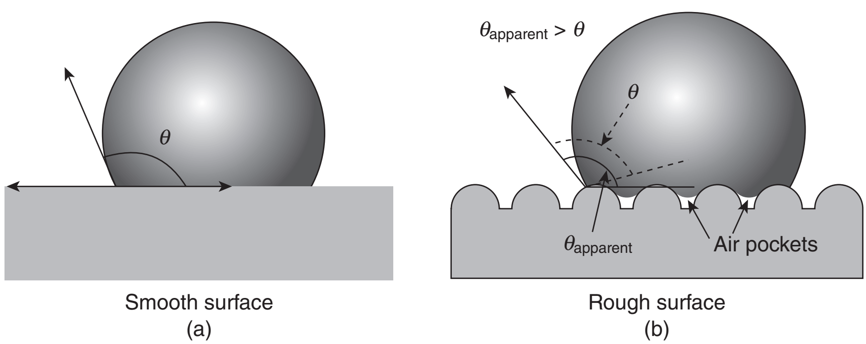
Surface coating with low surface energy coating materials has been the most common way to achieve a repellent surface with high water contact angle. Fluorinated polymer based materials have been known as the most effective hydrophobic coating materials. These include polytetrafluoroethylene (PTFE), fluoroalkysilanes, and perfluorinated polymers. These create low energy surfaces effectively (Ramaratnam *et al.*, 2008; Chaudhari *et al.*, 2005). Non-fluorinated polymers such as polystyrene have been utilized but they can impart only moderate hydrophobicity.

However, these traditional textile coating materials, which modulate surface energy alone, can hardly achieve enough hydrophobicity to create a self-cleaning surface where liquid droplets roll off from the surface as the result of extreme hydrophobicity. An extremely hydrophobic surface, where the water contact angle exceeds 150° is often called a superhydrophobic surface. Droplets on the superhydrophobic surface easily roll off by a slight tilting of the surface, typically less than 10° (Liu *et al.*, 2009b). This is commonly known as the Lotus effect, named after Lotus plants whose leaves

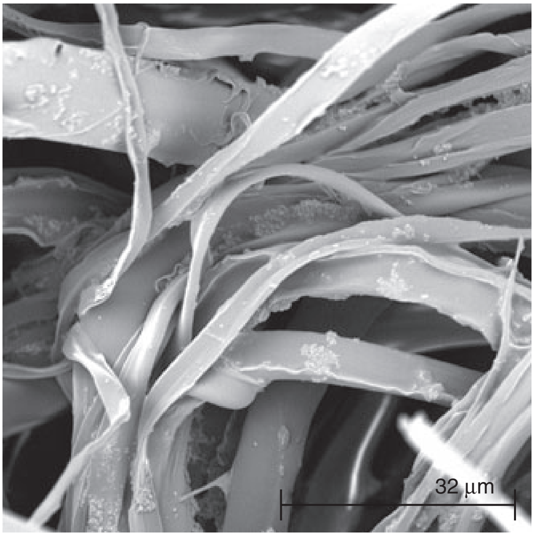
have high water repellency that make water droplets just roll off their surface, taking dirt along with them and always maintaining a clean appearance. This is caused by a combination of the hydrophobic surface character and micro-structural roughness (Elizalde and Schmit, 2010).

Engineering a superhydrophobic surface involves modifying both surface composition and geometry. It has been shown that a reduction of surface energy will not increase the contact angle to the regime of a superhydrophobic surface (Lafuma and Quere, 2003); the geometry or microtopology of the surface is the key to achieving this. Wetting of a rough surface is different from that of a smooth surface described by the Young's equation. For a hydrophobic surface, a droplet may not penetrate through indentations because droplets sit on air pockets trapped in the surface indentations underneath the droplet (Bhushan *et al.*, 2008; Marmur, 2004) (Fig. 3.10b). This creates a heterogeneous solid–air interface having a very high apparent contact angle and the drops become easy to remove (Cassie and Baxter, 1944; Bhushan *et al.*, 2008). The creation of a surface with nano/micro roughness to provide superhydrophobicity has been the subject of many research papers since the discovery of the lotus effect (Garcia *et al.*, 2004; Marmur, 2004; Wu *et al.*, 2004; Bhushan and Jung, 2007).

One way to use these phenomena to create superhydrophobic fabric surfaces is micro/nanoparticulate coating. Nano and microparticles are mixed with hydrophobic polymer and applied to the substrate to create micro-roughness on the fiber surface. An example of a surface of a microparticulate coated fiber is given in Fig. 3.11 (Shim, 2010b). It was shown that the nanoparticulate-incorporated hydrophobic coating effectively imparted superhydrophobicity to textile fabrics (Ramaratnam *et al.*, 2008). Such fabrics are already utilized in many different products, such as scrubs and



3.10 The effect of surface roughness on liquid repellency. (a) Droplet on a smooth surface, (b) droplet on a rough surface. θ is the contact angle and $\theta_{apparent}$ is the apparent contact angle. Both smooth and rough surfaces have identical θ.



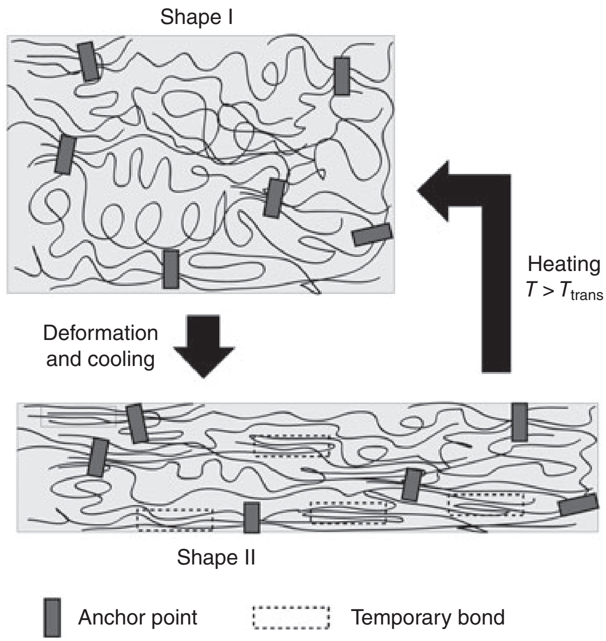
3.11 SEM image of microparticulate coated fiber surface (Shim, 2010b).

protective gowns, where high protection and self-cleaning abilities are required (Williamson, 2010).

3.3.3 Coatings with shape-memory polymers

A shape-memory polymer (SMP) is a material that 'memorizes' its permanent shape. It has the ability to recover this permanent shape from its temporary deformation under particular environmental conditions. On a molecular level, SMPs consist of soft and hard segments (Fig. 3.12). The hard segments (or net points) form bonds or anchor points (covalent bonds, physical attraction, etc.), so the permanent shape is maintained. The soft segments (or switch segments) possesses elasticity and have a tendency to recover from deformation. The soft segment phase transforms from the glassy or crystalline state to the rubbery state, depending on environmental conditions such as temperature, light, and solvent. Chains are free to recover their original shape as it transforms to the rubbery state, while the hard segment structure stays intact during the phase change of the soft segments. This structure can lead to unique shape-memory properties introduced by sequential processing (Hu and Zhuo, 2010).

The processing step to achieve the shape-memory effect consists of (i) extrusion/molding to a permanent shape and (ii) forming and stabilizing a temporary shape. If this material is exposed to environmental stimuli that cause phase changes of the soft segments, the permanent shape is recovered. The processing and recovery of a thermally responsive SMP polymer is illustrated in Fig. 3.12. First, an SMP is extruded and cooled to its permanent



3.12 Schematics of SMP structures and their shape memory effects.

shape (Shape I). At above the transition temperature, T_{trans} (which is often the T_g of the soft segment), the polymer is deformed to a temporary shape (Shape II). By cooling down below T_{trans}, the soft domains are frozen while they are stretched, so the temporary shape is formed and stabilized, and this temporary shape would be maintained while the temperature remains below T_{trans}. However, it still holds the memory of permanent shape in the hard segment conformation since the phase change temperature of the hard segment is far higher than that of the soft segment. On exposure to high temperature above T_{trans}, it recovers to its permanent shape (Shape I) by recovery of the soft segments (Meinander, 2005; Hu and Zhuo, 2010).

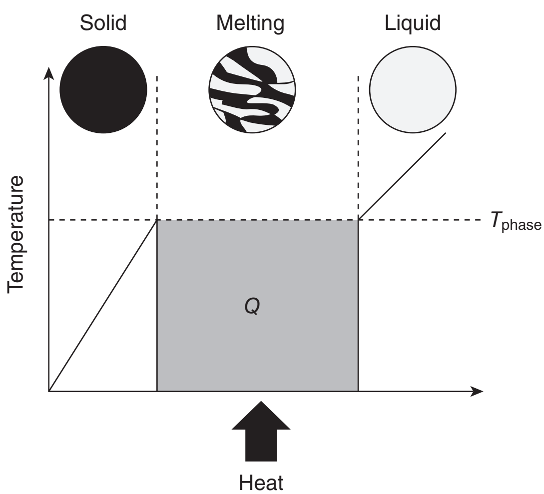
In textiles, SMPs can be added in coating and laminating and provide benefits in some potential applications such as wrinkle-free clothing (Chan Vili, 2007) and space components for insulation (Meinander, 2005). In medical textiles, there are intelligent surgical sutures that have self-knotting or tightening-on-demand properties (Lendlein, 2010).

Since change of the shape is caused by molecular structural changes, shape changes are often accompanied by other property changes such as diffusibility, transparency, refractive index, modulus, and permeability (Lendlein, 2010). These property changes can be used to engineer a smart barrier where the permeability of a fabric is altered by temperature or other stimuli. For example, below the transition temperature, an SMP becomes

rigid and it prevents permeation of water vapor molecules through active diffusion. Moisture permeability increases above T_{trans} as molecular motion of the soft segments becomes active. This creates an interesting temperature–water vapor transmission rate profile of the material, which can provide protection and comfort, with the ability to control breathability by temperature changes. For textiles treated with this type of material, moisture vapor permeability increases at high temperature and the human body is able to release heat and moisture through the fabric more easily. As permeability drops in a cold climate, the fabric does not allow moisture to escape and so prevents loss of body heat through evaporation (Mondal and Hu, 2007; Lendlein, 2010; Meinander, 2005; Chan Vili, 2007).

3.3.4 Coatings with phase-change materials for thermal insulation

Phase-change materials (PCMs) have a large amount of latent heat that can be released or absorbed while they undergo phase changes within narrow temperature ranges. As illustrated in Fig. 3.13, when the temperature reaches their phase change temperature, T_{phase} during a heating process, a phase change from solid to liquid occurs, and such phase changes absorb a large amount of latent heat, Q, while the temperature remains constant (Mondal, 2008; Meinander, 2005). During the cooling process, this heat is released at T_{phase} as the result of the phase change from liquid to solid. These materials have the ability to absorb and store a large amount of heat and stored heat can be released by cooling in a cold climate. The incorporation of PCMs in



3.13 Heat absorption by phase change polymer.

protective clothing could therefore improve thermal performance (Pause, 2010; Meinander, 2005).

For PCMs to be useful for protective garments, they should have (i) an appropriate phase-change temperature (close to room temperature range, 20–40 °C) and (ii) a large latent heat. The most used PCMs are paraffin-based materials such as eicosane, nonadecane, octadecane and heptadecane, and polyethylene glycol (PEG)-based materials.

Since these materials undergo phase changes from solid to liquid, they have to be applied in a way to prevent leakages from the system. The most common way to achieve this is micro-encapsulation. The PCM is first enclosed in very small spheres (microcapsules in the diameter range 1–20 μm) and these are then incorporated in a coating paste and applied to a fabric substrate (Pause, 2010; Meinander, 2005). Another method is crosslinking the PCM itself to a polymer matrix of the coating material. This method is cheaper and also enables the addition of more PCM for the same coating polymer amount, and so can provide higher latent heat capability as a result (Pause, 2010).

3.3.5 Conductive coatings

As described in Section 3.1, one critical part of building a smart protective clothing system is a component that transfers signals. This generally requires components with high conductivity for sensing, signal transmission, monitoring and actuation (Wang *et al.*, 2010; Meinander, 2005). Most textile-based materials are organic polymers; these are insulators that have little conductivity, so imparting conductivity to these materials is needed for development of a smart textile system.

Co-spinning with conductive particles during the spinning, or use of metal/carbon fibers in fabric production, are two ways of producing conductive fabrics. However, they both require a high concentration of conductive material to reach the required conductivity (Koncar *et al.*, 2007). Poor spinnability, processibility and deterioration of mechanical properties become problems in these techniques, in addition to the high cost associated with the need for a large amount of conductive filler, which is often expensive. Thus, conductive *coating* is most desirable and provides a cost-effective way to impart conductivity because a small amount of a conductive layer created by the coating is often sufficient to provide enough conductivity for the required applications (Wang *et al.*, 2010).

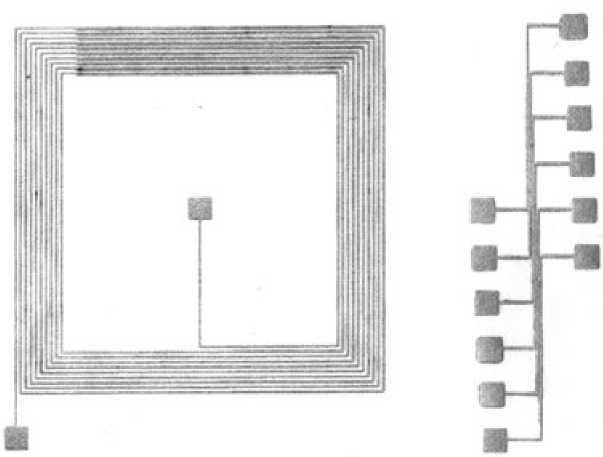
Conductive coatings (Liepins, 2001) include metal coatings, conductive polymer coatings and coating with a paste doped with a conductive filler. Metal deposition is mostly carried out, not by a conventional textile process, but by vacuum deposition, ion plating, electroplating or electroless plating. Some of these techniques are discussed in Section 3.4.

Conductive polymers are polymeric materials that conduct electricity, and their electrical properties are sensitive to external effects such as radiation, temperature and chemicals (Wang *et al.*, 2010). The most well-known conductive polymers are polypyrrole (PPy) (Meinander, 2005), polyaniline (PANI) (Koncar *et al.*, 2007), polythiophene, and their derivatives (Wang *et al.*, 2010). A coating paste consisting of microdispersed carbon or conductive particles in a polymer also can be used for conductive coatings. This configuration can be used in a sensor application, since a drastic change in electric resistance is obtained by mechanical deformation (Meinander, 2005).

Conductive printing is another interesting area in smart textiles. Printing technology is capable of producing complicated patterns on fabric structures and the use of it on fabric surfaces to create flexible circuits is attractive in building a smart textiles system (Karaguzel, 2006). Many different types of conductive inks are commercially available and they have conductive elements within their formulations, such as carbon, metals, and conductive polymers. It has been demonstrated that printing technology can create high resolution circuits by the use of conductive polymers (Fig. 3.14) (Karaguzel, 2006).

3.3.6 Functional and smart additives for coating applications

Coating materials used in textiles are typically polymeric materials, or their polymer precursors, in a carrying medium. They are highly formulated to achieve good processibility, firm adhesion to the substrate, and the



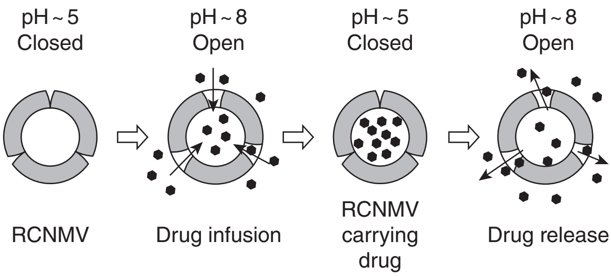
3.14 Conductive printing on nonwoven fabrics. (Source: Nonwovens Institute, North Carolina State University, USA.)

functionality desired (Shim, 2010a). Additives are frequently incorporated into basic coating formulations to impart color, opacity, antistatic properties and processibility. The most common additives are catalysts, flow modifiers, emulsifiers, wetting agents, UV stabilizers, flame retardant chemicals, heat stabilizers, antioxidants, fillers for mechanical property improvement, fillers for economy, pigments, and coupling or bonding agents to promote adhesion (Wicks *et al.*, 1999). Incorporation of additives in a basic coating formation opens up huge opportunities to create/engineer surface properties of textiles. Beyond the conventional coating additives mentioned above, novel materials can be easily added into coating formulations and many demonstrate the potential to create smart, protective textile systems.

One category extensively studied and continuously evolving is nanoparticles and nanofillers. As discussed previously (Section 3.3.2), superhydrophobicity has been achieved by nanoparticle incorporation in the coating formulation. Hybrid materials, such as polymer–clay nanocomposite, can also exhibit smart responses. Keszie *et al.* (2005) have reported a pH-responsive silicon-based coating incorporating montmorillonite (MMT) organoclay particles. At high pH, the distance between the clay layers swells and this induces volume increases. At lower pH, the layers are attached to each other, reduced the coating thickness.

Some nanoparticles can function by more than changing properties – they can provide adaptive properties. It has been reported that creation of a 'heat regenerating material' by incorporation of certain ceramic particles such as zirconium carbide, Group VIII transition metal oxides and TiO_2 has been achieved. These particles absorb light energy at short wavelengths and convert it into heat energy in the form of infrared radiation (Tao, 2001). As a result of this function of ceramic particles, a significant rise in fabric surface temperature on exposure to light has been found. (Tao, 2001).

Another type of additive that can be utilized in smart coatings is biological nanoparticles, such as viruses. Viruses can be seen as functional protein cages that have the ability to hold large amounts of active agents (Honarbakhsh, 2010; Loo *et al.*, 2007). Plant viruses, such as red clover necrotic mosaic virus, are attractive additives to incorporate in coatings as a smart nano-carrier to release active ingredients, including chemical compounds and drugs, when needed. They are inert to humans, as they are inherently not able to target human cells. Their size and shape – nanosize particles with uniform structures – and robustness in use and in processing, make it possible to use them in the functionalizing process. In addition, compared to other nano-particulate additives, a plant virus can be produced in plants or in plant bioreactors relatively inexpensively (Loo *et al.*, 2007; Honarbakhsh, 2010; Ochekpe *et al.*, 2009). Figure 3.15 illustrates the process of using red clover necrotic mosaic virus (RCNMV) as a nano-carrier (Sherman *et al.*, 2006; Ochekpe *et al.*, 2009; Franzen and Lommel, 2009). Its outer



3.15 Schematics of drug infusion and delivery process of a plant virus nano-carrier – red clover necrotic mosaic virus (RCNMV) (Franzen and Lommel, 2009; Honarbakhsh, 2010).

diameter is about 36.6 nm and an inner cavity is a diameter of about 17 nm. The inner cavity is accessible through surface pores (channels) (Honarbakhsh, 2010). These pores can be opened or closed as protein units in shells reorient in response to a change in pH and the presence of an ion. The pores of RCNMV are opened at pH ~ 8, whereas they are closed at pH ~ 5. Drug or other active agents can be infused through the open pores. After the pores are closed, the agents remain stored inside the virus nano-carrier until it encounters an appropriate environmental stimulus that opens the pores, and at this point, the active agent is released to perform its intended function (Loo *et al*., 2008).

Another way that additives contribute to smart protective systems is in the creation of a responsive interface. Flame retardant (FR) properties can be imparted in different ways, but simple surface treatments generally suffer from lack of durability. More durable flame retardancy can be achieved by the use of additives dispersed and locked in the polymer matrix during manufacturing and use. But for these additives to work effectively, the FR material needs to be delivered to the surface to act on the fire. Keszie *et al*., (2005) showed an interesting way to achieve this, using smart interfaces between additives and the polymer matrix. At normal temperatures, FR particles have compatibility with the host polymer matrix through a compatibilizing component that has affinity to the hydrocarbon host polymer matrix. It insures good processibility and mechanical properties during process and use. As the temperature rises in the fire, the compatibilizing groups are detached and the flame retardant particles migrate to the surface as the result of their loss of compatibility. Such a system would create a fire protective barrier at the surface.

3.4 Other surface treatment methods

Various traditional textile processes such as coating and grafting have been adapted successfully to functionalize textile surfaces for smart protective

fabrics as discussed in previous sections. These techniques have the ability to introduce various smart materials into textile structures and provide advantages in that they are industrially available. However, there are some limitations regarding processibility of new materials and the precise controls required in smart surface functionalization. Therefore, it is worthwhile to mention some surface treatment methods that are in the development stage or are used in other industries (Shim, 2010a). In this section, various methods which are not conventionally used in textile surface modification but have potential for advanced applications are discussed.

3.4.1 Plasma surface treatment

Plasma is often referred to the fourth state of matter, after solid, liquid and gas. Plasma is the mixture of partially and fully ionized gas, photons, free electrons, and chemically reactive atoms and radicals (Yang *et al*., 2007; Buyle *et al*., 2010; Cornelius, 2009). Even though it is highly ionized, plasma is on average, electrically neutral. Plasma is created by raising the energy content of matter through various techniques, such as corona discharge, dielectric barrier discharge, glow discharge or the application of a high electric field. When the kinetic energy of gas molecules exceeds their ionization energy, the outermost electrons of the gas molecules escape from the electron cloud and the molecules become ionized. Since plasma can provide a high concentration of active species, it interacts with the substrate surface and initiates various chemical reactions. Most species in plasma interact only with the outermost surface of the substrate as its interaction depth is limited to about 10 nm or less. Therefore, plasma is a highly surface specific treatment and does not alter substrate bulk properties.

The nature of interaction between plasma and substrate can be complicated and different types of plasma, the energy and active specie, and presence of other chemical compounds results in diverse reactions. A variety of reactions is possible and these include surface etching, smoothing, deposition, scission, cross-linking, surface roughening, and grafting (Cornelius, 2009).

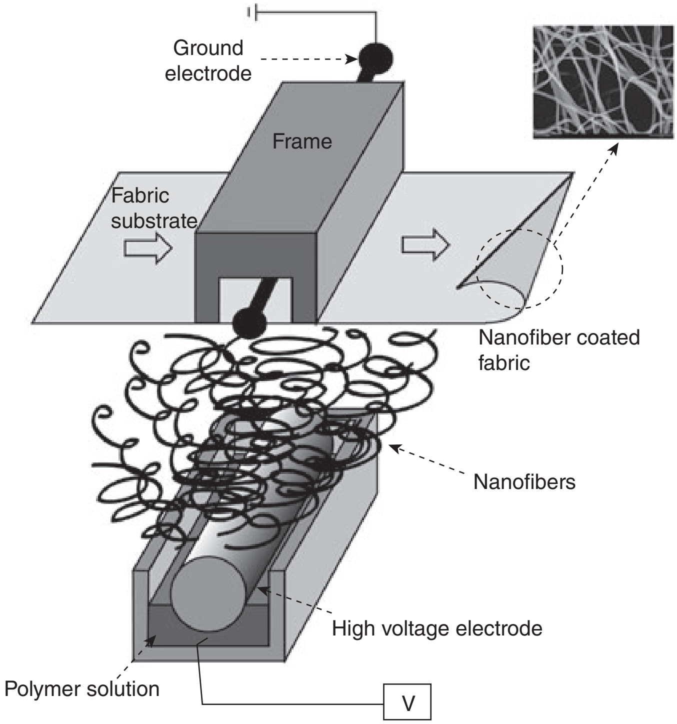
Plasma is widely used in surface treatments in various industries and it has been reported that plasma treatment can be used to modify the surface properties of textile materials. Possible applications include imparting hydrophilicity, enhancing hydrophobicity, increasing adhesion, changing electrical conductivity, enhancing dyeability and printability, and color-depth enhancement. The use of plasma treatment for antibacterial finishes, fire retardant finishes and sterilization have also been reported (Wei, 2009; Buyle *et al*., 2010; Cornelius, 2009). Plasma treatment has been recognized as a possible substitute for many textile wet processes that consume high energy and water.

3.4.2 Nanofiber coating via electrospinning

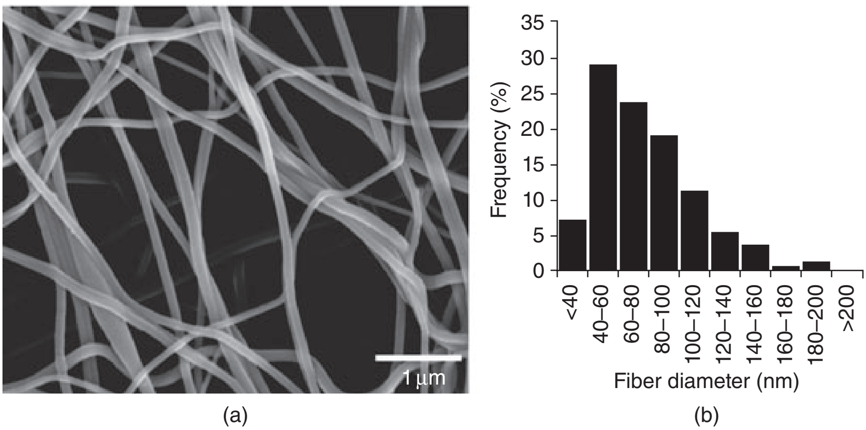
Most of the coating techniques described previously have involved deposition of thin films on the surface of fibers or fabrics, whether monolithic or microporous. Compared with these coating layers, the formation of a nanoscale fibrous coating layer has advantages because it can provide very high surface-area-to-volume ratio and interconnected micro/nano pore networks. It enhances hydrophobicity through its multiscale nanotexture and air filled pores, so it is a good material for breathable barriers (Lembach *et al.*, 2010). Use of nanofiber layers can be beneficial in applications such as nanoparticle filtration (Yeom *et al.*, 2010), purifications and decontaminations, scaffolds in tissue engineering (Li *et al.*, 2002), drug delivery (Honarbakhsh, 2010) and carriers of catalysts.

Even with recent advances, nanofiber production is a relatively slow process compared with traditional textile processes. In addition to low productivity, limited mechanical properties and drastic permeability loss in thick nano-fiber layers can limit the use of stand-alone nanofiber fabrics. Therefore, they are not economically attractive in most applications. However, interestingly, a thin layer of nanofibers deposited on a fabric surface can impart unique properties, including drastic improvement in barrier and filtration performance, changes of surface repellency and thermal and acoustic insulations. So, a thin layer of nanofiber coating is economically advantageous over nanofiber fabrics.

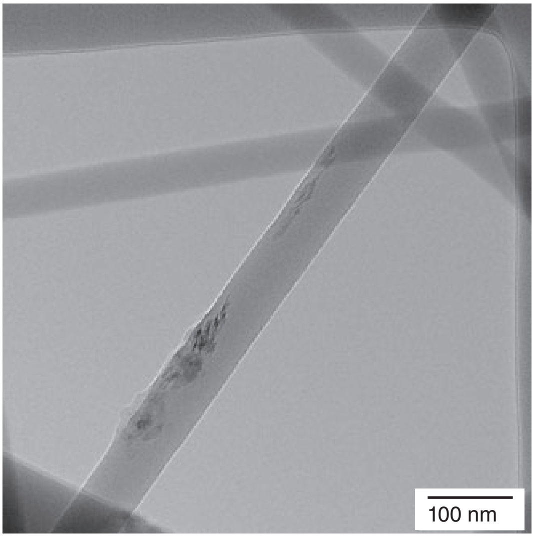
Nanofiber production methods are continuously evolving; the most common method is electrospinning, where nano-size fibers are formed by electrostatic forces pulling a polymer solution jet. Direct electrospinning on a substrate forms a coating layer of nanofibers on the surface of the substrate (Heikkila *et al.*, 2007). Electrospinning (and other nanofiber formation methods) has been developed and expanded tremendously during the last decade and it is being moved from laboratory scale to commercial scale (Andrady, 2008). One example of these commercial systems, is 'nanospider™' (Elmarco), which can produce nanofibers with diameters, of about 50 nm through continuous needle-less electrospinning. A schematic for making a nanofiber coating on a fabric substrate with a needle-less electrospinning system is illustrated in Fig. 3.16 (Yeom *et al.*, 2010). An electric film, formed between a high voltage electrode and a ground electrode, pulls a polymer solution (either film or droplets) to form a so-called Taylor cone which becomes a stable jet and eventually leads to a fibrous web on substrate. Figure 3.17 shows an SEM image of a nylon 6 nanofiber layer and its fiber diameter distribution, produced with an Elmarco nanospider (Yeom *et al.*, 2010). Fiber formation and fiber size distribution depend on polymer solution parameters such as molecular weight, solution viscosity and conductivity; and on processing parameters such as applied potential,



3.16 Nanofiber coating with a needle-less electrospinning system (Yeom *et al.*, 2010).



3.17 (a) SEM image of PA6 nanofibers and (b) their fiber diameter distribution (Yeom *et al.*, 2010).



3.18 TEM image of nanofiber with nanoparticle additives (Yeom *et al.*, 2010).

collector type and gap distance and solution supplying method (Andrady, 2008). It has been demonstrated that various polymers, such as PA6, poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO) and poly(vinylidene fluoride) (PVDF), can form nanofibers effectively through electrospinning (Yeom *et al.*, 2010). Nanoparticle additives can be easily added and impart further functionality. Figure 3.18 shows an example of nanofiber with nanoparticle additives (Yeom *et al.*, 2010).

3.4.3 Thin film deposition

Various thin film deposition techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD), and electroless plating are available to create a nanolayer on a substrate. Even though these are not commonly used in textile processing, they are worth mentioning because (i) they make it possible to incorporate nonconventional materials in a textile system and (ii) they provide the ability to create nanolayers and nanofabrications (Wei, 2009).

In physical vapor deposition (PVD), vaporized material is transferred to the substrate surface and deposits as a thin film (Mattox, 1998). Vaporization is achieved by the use of evaporation by heating or an electron-beam, sputtering or laser ablation (Martín-Palma and Lakhtakia, 2010). This is generally performed in a vacuum. PVD of metals and metal oxides on polymers has shown enhancement of oxygen and water vapor barrier properties (Spagnola, 2010; Leterrier, 2003).

CVD is where the surface of a substrate is modified by depositing layers via chemical reactions in a gaseous medium (Bhat, 2001). One or more volatile precursor materials are decomposed and/or reacted on the substrate surface to deposit a thin film. Many different types of CVD systems are available that utilize thermal, laser and plasma energies, and wide ranges of chamber pressures are possible, from atmospheric pressure to ultrahigh vacuum, in this process (Martín-Palma and Lakhtakia, 2010).

ALD is another vapor phase film deposition technique that can create thin conformal deposition through sequential, self-limiting surface reactions (George, 2010). Vapor phase film precursors react only with the available reaction site and no more reaction occurs after the surface is saturated, so, film growth rate is independent of the amount of precursor available (Spagnola, 2010). Because of this self-limiting film growth mechanism, ALD has the advantages of precise thickness control at monolayer level, production of sharp interfaces, uniformity over large areas, excellent conformability with the substrate, good reproducibility, multilayer processing capability, and desirable film qualities at relatively low temperatures (Martín-Palma and Lakhtakia, 2010; George, 2010).

3.4.4 Sol–gel technique

Sol–gel technology has been used to fabricate ceramics, glass and metal oxides. The process starts with precursor materials forming the 'sol' phase. It is in this liquid phase (such as a colloidal form) that coating or deposition on the substrate can be carried out. Additives can be easily mixed and uniformly distributed. Then, it undergoes gelation, where the precursor materials transfer from a liquid 'sol' to solid 'gel' form (Haufe *et al*., 2005; Innocenzi, 2008). Sol–gel technology is used for applications such as optics, protective and porous films, optical coatings, window insulators, dielectric and electronic coatings, high temperature superconductors, reinforcement fibers, fillers, and catalysts (Innocenzi, 2008).

Sol–gel technology is capable of producing a wide variety of forms of materials, including nanostructure materials such as nanoparticles, nanofibers and microporous inorganic membranes. Use of a nano-dispersion of the precursor (nano-sol) can create interesting nanostructured materials through the sol–gel process. Various nano-sol processes have been investigated using silica and metal oxide based nano-sols and it has been reported they can be used for improved fiber heat resistance, create hydrophilic and hydrophobic surfaces (Textor and Mahltig, 2010; Mai and Militz, 2004; Haufe *et al*., 2005), oleophobicity and soil repellency (Satoh *et al*., 2004; Fabbri *et al*., 2006) and be used for embedding conductive filler in the oxide matrix. They can also be used to incorporate bioactive compounds

(Bottcher *et al*., 2004) and change light absorption properties (applications such as solar cells or UV protection) (Haufe *et al*., 2005)

3.5 Conclusion and future trends

Surface treatments are one of the most effective ways to impart functionality to textiles and fibers. As the surface plays a critical role in smart and protective clothing, surface treatment is an essential part of building a smart and protective fabric system. The surface is where the material first responds and interacts with the environment. Ideally, the smart protective surface will sense the various environmental hazards – thermal, radiation, or chemical in nature – and respond to block them from harming the human body while not interfering with moisture and air interchange, to provide comfort.

Various surface treatment methods have been introduced to impart smart adaptive properties for protective systems. The polymer brush system has gained considerable interest as it can achieve drastic surface modification through chain conformation changes. It is possible to engineer surfaces to react to specific stimuli through different polymer types and utilization of copolymers to form mixed brush systems. In addition, most of the reactions are reversible.

Coating is another technology that can be utilized to create smart surfaces for protective clothing. It is one of the oldest methods to impart functionality to textiles, many different coating processes having been developed to handle wide ranges of coating materials and substrates. Various smart materials such as phase-change polymers, shape-memory polymer, nanoparticles, and conductive materials can be introduced to textile systems through coating technology without significant investment in infrastructure or additional processing cost.

Other novel techniques, such as nanolayer deposition and nanofiber coatings, have been recognized as potential tools to create smart functional surfaces due to their ability to incorporate various non-traditional materials and to control morphology and thickness more precisely.

3.6 Sources of further information and advice

Corriu R and Nguyên T A (2009), *Molecular Chemistry of Sol–Gel Derived Nanomaterials*, Chichester, U.K, Wiley.

Edmondson G K and Benisek L (1981), 'Protective clothing fabrics', *Textile Research Journal*, 51(3), 182–190.

Ercole F, Davis T P and Evans R A (2010), 'Photo-responsive systems and biomaterials: photochromic polymers, light-triggered self-assembly, surface modification, fluorescence modulation and beyond', *Polymer Chemistry*, 1(1), 37.

Fedorko P, Miusik M, Nedelev T, Krupa I, Olejinkova K, Omastova M, and Chehimi M M (2007), 'Conductive polymer-coated textiles: the role of fabric treatment by pyrrole-functionalized triethoxysilane', *Synthetic Metals*, 157(22–23), 914–923.

Fong, H and Reneker D H (2006), *Polymeric Nanofibers*, Washington, DC, American Chemical Society: Distributed by Oxford University Press, UK.

Fu G-D, Iu L-Q, Yao F, Li G-L, and Kang E-T (2009), 'Smart nanofibers with a photoresponsive surface for controlled release', *ACS Applied Materials & Interfaces*, 1(11), 2424–2427.

Fundueanu G, Constantin M, Nichifor M, Branisteanu D, Mocanu G, Costuleanu M, and Radu C D (2009), 'New multifunctional textile biomaterials for the treatment of leg venous insufficiency', *Journal of Materials Science: Materials in Medicine*, 20(4), 975–982.

Garcia A A, Picraux S T, Taraci J L, Clement T, Daily J W, Rosario R, Gust D, and Hayes M (2004), 'Lotus effect amplifies light-induced contact angle switching', *Journal of Physical Chemistry B*, 108(34), 12640–12642.

Ghosh S K (2006), *Functional Coatings : By Polymer Microencapsulation*, Weinheim, Wiley-VCH, John Wiley.

Guimond S, Amberg M, Hanselmann B, and Hegemann D (2010), 'Plasma functionalization of textiles: specifics and possibilities', *Pure and Applied Chemistry*, 82(6), 1239–1245.

Higuchi A, Hamamura A, Shindo Y, Kitamura H, Yoon B O, Mori T, Uyama T, and Umezawa A (2004), 'Photon-modulated changes of cell attachments on poly(spiropyran-co-methyl methacrylate) membranes', *Biomacromolecules*, 5(5), 1770–1774.

Hu Z, Cai T, and Chi C (2010), 'Thermoresponsive oligo(ethylene glycol) methacrylate-based polymers and microgels', *Soft Matter*, 6(10), 2115.

Jamrozpiegza M, Utratawesolek A, Trzebicka B, and Dworak A (2006), 'Hydrophobic modification of high molar mass polyglycidol to thermosensitive polymers', *European Polymer Journal*, 42(10), 2497–2506.

Kabanov V Y (2000), Radiation chemistry of smart polymers (A review). *High Energy Chemistry*, 34(4), 203–211.

Kichigina G A, Kiryukhin D P, Buznik V M, Bolshakov A I, Prorokova N P, Kumeeva T Y, and Khorev A V (2010), 'Giving polyester textile materials high water repellency by treating them with a solution of tetrafluoroethylene telomers', *Fibre Chemistry*, 42(2), 103–108.

Kiekens P and Pastore C M (2001), *Surface Characteristics of Fibers and Textiles*, New York, Marcel Dekker.

Klein L C (1988), *Sol–Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes*, Park Ridge, N.J., USA, Noyes Publications.

Lewandowski M, Cochrane C, Koncar V, Boussu F, and Dufour C (2009), 'Electro-conductive sensors and heating elements based on conductive polymer composites', *International Journal of Clothing Science and Technology*, 21(2–3), 82–92.

Luca C, Grigoriu A M, and Grigoriu A (2008), 'UV protective treatments of cellulose materials with beta-cyclodextrine derivatives', Revista de Chimie 59(5), 569–574.

Muller H, Oehr C, and Vohrer U (1998), 'Glow-discharge treatment for the modification of textiles', *Surface and Coatings Technology*, 98(1–3), 1128–1131.

Oettel J, Mohring U, and Neudeck A (2010), 'Coating of electro conductive textile structures', Tekstil 59(8), 364–365.

Padday J F (1978), *Wetting, Spreading, and Adhesion*, London, Academic Press.

Provder T and Baghdachi J (2009), *Smart Coatings II*, New York, Oxford University Press.

Reneker D H and Yarin A L (2008), 'Electrospinning jets and polymer nanofibers', *Polymer*, 49(10), 2387–2425.

Russell T P (2002), Surface-responsive materials. *Science*, 297(5583), 964–967.

Saranya B, Deepa P, Anikumar A, Karthika R, Maheshwari N, Nimala Devi A S, and Perumalraj R (2011), ' Silver-filled electrically conductive epoxy and silver nitrate-plated textile composite materials for EMC', *Journal of Reinforced Plastics and Composites*, 30(3), 203–215.

Ulrich C (2006), 'Nano-textiles are engineering a safer world'. *Human Ecology*, 34(2), 2.

Van der Schueren L, and De Clerck K (2010), 'The use of pH-indicator dyes for pH-sensitive textile materials'. *Textile Research Journal*, 80(7), 590–603.

Voyer J, Schreiber M, and Schulz P (2008), 'Electrically conductive flame sprayed aluminum coatings on textile substrates', *Journal of Thermal Spray Technology*, 17(5), 818–823.

Wang S, Song Y, and Jiang L (2007), 'Photoresponsive surfaces with controllable wettability', *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 8(1), 18–29.

Wang X, Qing G, Jian L, Fuchs H, and Sun T (2009), 'Smart surface of water-induced superhydrophobicity', *Chemical Communications*, (19), 2658.

Wei Q (2009), *Surface Modification of Textiles*, Boca Raton, FL, CRC Press and Cambridge, UK, Woodhead Publishing, in association with the Textile Institute.

Wischerhoff E, Badi N, Lutz J-F, and Laschewsky A (2010). 'Smart bioactive surfaces'. *Soft Matter*, 6(4), 705.

Xia F, Zhu Y, Feng L, and Jiang L (2009), 'Smart responsive surfaces switching reversibly between super-hydrophobicity and super-hydrophilicity', *Soft Matter*, 5(2), 275.

Xiao C, Wang Y, An S, Jin X, and Jia G (2006), 'Preparation and properties of a new coating method for preparing conductive polyester fibers with permanent conductivity'. *Journal of Applied Polymer Science*, 102(3), 2685–2691.

Xu Z.-K (2009). *Surface Engineering of Polymer Membranes*, New York, Springer.

Yan X T and Xu Y (2010), *Chemical Vapour Deposition: An Integrated Engineering Design for Advanced Materials*, Springer Verlag.

Yoo S and Barker R L (2005), 'Comfort properties of heat resistant protective workwear in varying conditions of physical activity and environment. Part II: Perceived comfort response to garments and its relationship to fabric properties', *Textile Research Journal*, 75(7), 531–539.

Zhou F and Huck W T S (2006), 'Surface grafted polymer brushes as ideal building blocks for smart surfaces', *Physical Chemistry Chemical Physics*, 8(33), 3815.

Zhou J, Wang G Hu J, Lu X, and Li J (2006), 'Temperature, ionic strength and pH induced electrochemical switching of smart polymer interfaces', *Chemical Communications*, (46), 4820.

3.7 References

Adamson A W and Gast A P (1997), *Physical Chemistry of Surfaces* 6th ed., New York, Wiley.

Advincula R C (2004), *Polymer Brushes: Synthesis, Characterization, Applications*, Weinheim, Wiley-VCH.

Andrady A L (2008), *Science and Technology of Polymer Nanofibers*, Hoboken, N.J., Wiley.

Bhat D G (2001), Chapter 32. 'Chemical Vapor Deposition', in Satas D and Tracton A A, *Coatings Technology Handbook*, New York, Marcel Dekker, Inc., 313–325.

Bhushan B, Nosonovsky M and Jung Y C (2008), Chapter 19. 'Lotus effect: roughness-induced superhydrophobic surfaces', in Bhushan B (eds.), *Nanotribology and Nanomechanics: An Introduction*, Berlin, Springer.

Bhushan B and Jung Y C (2007), 'Wetting study of patterned surfaces for superhydrophobicity', *Ultramicroscopy*, 107(10–11), 1033–1041.

Bitz K (2005), 'The best of both worlds', *Nonwovens Industry*, August.

Bottcher H, Soltmann U, Mertig M and Pompe W (2004), 'Biocers: ceramics with incorporated microorganisms for biocatalytic, biosorptive and functional materials development', *Journal of Materials Chemistry*, 14(14), 2176–2188.

Buyle, G, Perucca M, and Rauscher H (2010) *Plasma Technology for Hyperfunctional Surfaces: Food, Biomedical and Textile Applications*, Weinheim, Wiley-VCH.

Carrillo F, Defays B, and Colom X (2008), 'Surface modification of lyocell fibres by graft copolymerization of thermo-sensitive poly-N-isopropylacrylamide', *European Polymer Journal*, 44(12), 4020–4028.
Cassie A B D and Baxter S (1944), 'Wettability of porous surfaces', *Transactions of the Faraday Society*, 40, 546.
Chan Vili, Y Y F (2007), 'Investigating smart textiles based on shape memory materials', *Textile Research Journal*, 77(5), 290–300.
Chaudhari S S, Sankhe M D, Mathur M R, and De P (2005), 'UV-resist, water-repellent breathable fabric as protective textiles', *Journal of Industrial Textiles*, 34(4), 209–222.
Chen K S, Tsai J C, Chou C W, Yang M R and Yang J M (2002), 'Effects of additives on the photo-induced grafting polymerization of N-isopropylacrylamide gel onto PET film and PP nonwoven fabric surface', *Materials Science and Engineering: C*, 20(1–2), 203–208.
Cornelius C E (2009), *Novel Applications of Atmospheric Pressure Plasma on Textile Materials*, PhD Thesis, North Carolina State University. Raleigh, NC.
Ding X M, Hu J L, Tao X M, and Hu C P (2006), 'Preparation of temperature-sensitive polyurethanes for smart textiles', *Textile Research Journal*, 76(5), 406.
Dyer D (2006), 'Photoinitiated synthesis of grafted polymers, *Surface-initiated Polymerization*, I, 47–65.
Edahiro J, Sumaru K, Tada Y, Ohi K, Takagi T, Kameda M, Shinbo T, Kanamori T, and Yoshimi Y (2005), '*In situ* control of cell adhesion using photoresponsive culture surface', *Biomacromolecules*, 6(2), 970–974.
Edmondson S, Osborne V L, and Huck, W T S (2004), 'Polymer brushes via surface-initiated polymerizations', *Chemical Society Reviews*, 33(1), 14.
Elizalde O and Schmit M (2010), Chapter 14. 'Washpermanent nano-structured textiles', in J. Baghdachi and T. Provder, (eds.), *Smart Coatings III*. The ACS Symposium series, American Chemical Society.
Fabbri P. *et al.* (2006), 'Perfluoropolyether – based organic-inorganic hybrid coatings', *Polymer*, 47(4), 1055–1062.
Fidalgo L M *et al.* (2009), 'Polymer brush resist for responsive wettability', *Soft Matter*, 5(14), 2738–2745.
Franzen S and Lommel S A (2009), 'Targeting cancer with 'smart bombs': equipping plant virus nanoparticles for a 'seek and destroy'mission', *Nanomedicine*, 4(5), 575–588.
Fung W (2002), *Coated and Laminated Textiles*, Cambridge, England, Woodhead Publishing.
Garcia A A *et al.* (2004), 'Lotus effect amplifies light-induced contact angle switching', *Journal of Physical Chemistry B*, 108(34), 12640–12642.
George, S M (2010), 'Atomic layer deposition: an overview', *Chemical Reviews*, 110(1), 111–131.
Glawe A, Reuscher R, Koppe R, and Kolbusch T (2003), 'Hot melt application for functional compounds on technical textiles', *Journal of Industrial Textiles*, 33, 85–92.
Goossens F A (2001), Chapter19. 'Rotary Screen Coating', in Satas D and Tracton A A, *Coatings Technology Handbook*, New York, Marcel Dekker, Inc., 179–183.
Grant R R (1981), 'Coating and laminating applied to new product development', *Journal of Industrial Textiles*, 10, 232.

Greer R and Stelling P (1994), 'Application equipment for radiation curable coatings', *Journal of Industrial Textiles*, 24(1), 40.

Haufe H, Böttcher H, and Mahltig B (2005), 'Functionalisation of textiles by inorganic sol–gel coatings', *Journal of Materials Chemistry*, 15(41), 4385–4398.

He D, Susanto H, and Ulbricht M (2009), 'Photo-irradiation for preparation, modification and stimulation of polymeric membranes'. *Progress in Polymer Science*, 34(1), 62–98.

Heikkila P, Sipila A, Peltola M, Harlin A, and Taipale A (2007), 'Electrospun PA-66 coating on textile surfaces', *Textile Research Journal*, 77, 864–870.

Hewson R W, Kapur N, and Gaskell P H (2006), 'A theoretical and experimental investigation of tri-helical gravure roll coating', *Chemical Engineering Science*, 61, 5487–5499.

Higuchi A, Hamamura A, Shindo Y, Kitamura H, Yoon B O, Mori T, Uyama T, and Uemzawa, A (2004), 'Photon-modulated changes of cell attachments on poly(spiropyran-co-methyl methacrylate) membranes', *Biomacromolecules*, 5(5), 1770–1774.

Honarbakhsh, S. (2010), *Polymer-based Nanofibers Impregnated with Drug Infused Plant Virus Particles as a Responsive Fabric for Therapeutic Delivery*. PhD Thesis, North Carolina State University. Raleigh, NC.

Hu J and Zhuo H (2010), Chapter 8. 'Shape memory polymers in coating and laminates for textiles', in W. C. Smith (ed.) *Smart Textile Coatings and Laminates*. Cambridge, UK, Woodhead Publishing, in association with The Textile Institute and Boca Raton, FL, CRC Press.

Innocenzi P (2008), *Sol–gel Methods for Materials Processing: Focusing on Materials for Pollution Control, Water Purification, and Soil Remediation*, Springer Verlag.

Jarrell C (1992), 'A new process for coating and laminating face-finished fabrics', *Journal of Industrial Textiles*, 21, 212.

Jassal M and Agrawal A K (2010), Chapter 7. 'Intelligent breathable coatings and laminates for textile applications', in W. C Smith (ed.) *Smart Textile Coatings and Laminates*. Cambridge, UK, Woodhead Publishing, in association with The Textile Institute and Boca Raton, FL, CRC Press.

Karaguzel B (2006) *Printing Conductive Inks on Nonwovens: Challenges and Opportunities*, PhD Thesis, Raleigh, NC: North Carolina State University.

Kauffman G B and Seymour R B (1990), 'Elastomers: I. Natural rubber', *Journal of Chemical Education*, 67(5), 422.

Keeley V E (1991), 'Transfer coating with polyurethanes', *Journal of Coated Fabrics*, 20, 176.

Keszei S *et al*. (2005), 'Progress in interface modifications: from compatibilization to adaptive and smart interphases', *European Polymer Journal*, 41(4), 697–705.

Kim J B, Huang W, Bruening M L, and Baker G L (2002), 'Synthesis of triblock copolymer brushes by surface-initiated atom transfer radical polymerization', *Macromolecules*, 35(14), 5410–5416.

Koncar V, Saihi D, Devaux E, Campagne C, Kim B, Roux C, and Rochery M (2007), 'Processing and characterization of conductive yarns by coating or bulk treatment for smart textile applications', *Transactions of the Institute of Measurement & Control*, 29(3–4), 355–376.

Kopeček J (2007), 'Hydrogel biomaterials: a smart future?', *Biomaterials*, 28(34), 5185–5192.

Kumar V M, Schneider K, Nandan B, and Stamm M (2008), ‘ Switching of friction by binary polymer brushes’, *Soft Matter*, 4(5), 1024.

Lafuma A. and Quere D (2003), ‘Superhydrophobic states’, *Nature Materials*, 2(7), 457–460.

Lembach A N, Tan H-B, Roisman I V, Gambaryan-Roisman T, Zhang Y, Tropea C, and Yarn A L (2010), ‘Drop impact, spreading, splashing, and penetration into electrospun nanofiber mats’, *Langmuir*, 26(12), 9516–9523.

Lendlein A (2010), *Shape-memory Polymers*, New York, Springer.

Leterrier Y (2003), ‘Durability of nanosized oxygen-barrier coatings on polymers’, *Progress in Materials Science*, 48(1), 1–55.

Li W J, Laurencin C T, Caterson E J, Tuan R S, and Ko F K (2002), ‘Electrospun nanofibrous structure: a novel scaffold for tissue engineering’, *Journal of Biomedical Materials Research*, 60(4), 613–621.

Licari J J (2003), *Coating Materials for Electronic Applications – Polymers, Processes, Reliability*, *Testing*. Norwich, William Andrew Publishing.

Liepins R (2001), Chapter 81. ‘Conductive coatings’, in Satas D and Tracton A A, *Coatings Technology Handbook*, New York, Marcel Dekker, Inc., 711–720.

Lin S Y, Chen K S and Run-Chu L (1999), ‘ Thermal micro ATR/FT–IR spectroscopic system for quantitative study of the molecular structure of poly (N-isopropylacrylamide) in water’, *Polymer*, 40(10), 2619–2624.

Liu B, Hu J, and Meng Q (2009a), ‘Nonwoven supported temperature-sensitive poly (N-isopropylacrylamide)/polyurethane copolymer hydrogel with antibacterial activity’, *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 89(1), 1–8.

Liu Y, Chen X, and Xin J H (2009b), ‘Can superhydrophobic surfaces repel hot water?’, *Journal of Materials Chemistry*, 19(31), 5602.

Loo L N, Guenther R H, Lommel S A, and Franzen S (2008), ‘Infusion of dye molecules into red clover necrotic mosaic virus’, *Chemical Communications*, (1), 88–90.

Loo L N, Guenther R H, Lommel S A, and Franzen S (2007), ‘Encapsidation of nanoparticles by red clover necrotic mosaic virus’, *Journal of the American Chemical Society*, 129(36), 11111–11117.

Lutz J F, Akdemir Ö, and Hoth A (2006), ‘Point by point comparison of two thermosensitive polymers exhibiting a similar LCST: Is the age of poly (NIPAM) over?’, *Journal of the American Chemical Society*, 128(40), 13046–13047.

Luzinov I, Minko S, and Tsukruk V V (2004), ‘Adaptive and responsive surfaces through controlled reorganization of interfacial polymer layers’, *Progress in Polymer Science*, 29(7), 635–698.

Mai C and Militz H (2004), ‘Modification of wood with silicon compounds. inorganic silicon compounds and sol–gel systems: a review’, *Wood Science and Technology*, 37(5), 339–348.

Marmur A (2004), ‘The Lotus effect: superhydrophobicity and metastability’, *Langmuir*, 20(9), 3517–3519.

Martín-Palma R J and Lakhtakia A (2010), *Nanotechnology: A Crash Course*, Bellingham, WA, SPIE.

Mattox D M (1998), Handbook of Physical Vapor Deposition (PVD) Processing, Westwood, NJ, Noyes Publications.

Meinander H (2005), Chapter 7. 'Smart and intelligent textiles and fibers', in Shishoo R (ed.) *Textiles in Sport*. Cambridge, UK, Woodhead Publishing in association with The Textile Institute and Boca Raton, FL, CRC Press.

Mendes P M (2008), 'Stimuli-responsive surfaces for bio-applications', *Chemical Society Reviews*, 37(11), 2512.

Merlitz H, He G-L, Wu, C-X, and Sommer J-U (2009), 'Nanoscale brushes: how to build a smart surface coating', *Physical Review Letters*, 102(11), 115702.

Milner S T (1991), 'Polymer brushes', *Science*, 251(4996), 905–914.

Mondal S and Hu J L (2007), 'Water vapor permeability of cotton fabrics coated with shape memory polyurethane', *Carbohydrate Polymers*, 67(3), 282–287.

Mondal, S. (2008). Phase change materials for smart textiles – An overview. *Applied Thermal Engineering*, 28(11–12), pp. 1536–1550.

Ochekpe N A, Olorunfemi P O, and Ngwuluka N C (2009), 'Nanotechnology and drug delivery Part 2: Nanostructures for drug delivery', *Tropical Journal of Pharmaceutical Research*, 8(3), 275–287.

Park J-W, Kim H, and Han M (2010), 'Polymeric self-assembled monolayers derived from surface-active copolymers: a modular approach to functionalized surfaces', *Chemical Society Reviews*, 39(8), 2935.

Paul S (2009), *Surface Modification of Polypropylene Nonwovens to Improve Adhesion to Elastomers*. PhD Thesis. Raleigh, NC: North Carolina State University.

Pause B (2010), Chapter 9. 'Phase change materials and their application in coatings and laminates for textiles', in W. C. Smith (ed.), *Smart Textile Coatings and Laminates*. Cambridge, UK, Woodhead Publishing in association with The Textile Institute, and Boca Raton, FL, CRC Press.

Raheel M (1994), *Protective Clothing Systems and Materials*, New York, Marcel Dekker, Inc.

Ramaratnam K, Chumanov G, Iyer S K, Kinnan M K, Luzinov I, and Brown P J (2008), 'Ultrahydrophobic textiles using nanoparticles: lotus approach', *Journal of Engineered Fibers and Fabrics*, 3(4), 1–14.

Reynolds P (2005), Chapter 9. 'Wetting of surfaces', in Cosgrove T (ed.), *Colloid Science: Theory, Methods and Applications*. Ames, Iowa, Blackwell Publishing Professional.

Russell T P (2002), 'Surface-responsive materials', *Science*, 297(5583), 964–967.

Ryan A J, Croock C J, Howse J R, Topham P, Jones R A L, Geoghegan M, Parnell A J, Ruiz-Prez L, Martin S J, Cadby A, Menelle A, Webster J R P, Gleeson A J and Bras W (2005), 'Responsive brushes and gels as components of soft nanotechnology', *Faraday Discussions*, 128, 55.

Satoh K, Nakazumi H and Morita M (2004), 'Novel fluorinated inorganic–organic finishing materials for nylon carpeting', *Textile Research Journal*, 74(12), 1079–1084.

Scott R A (1995), Chapter 7. 'Coated and laminated fabrics', in Carr, C M (ed.), *Chemistry of the Textiles Industry*. London, Blackie Academic & Professional, 210–248.

Sen A K (2008), *Coated Textiles*, Boca Raton, FL, CRC Press.

Sherman M B, Guenther R H, Tama F, Sit T L, Brooks C L, Mikhailov A M, Orlova E V, Baker T S, and Lommel S A (2006), 'Removal of divalent cations induces structural transitions in red clover necrotic mosaic virus, revealing a potential mechanism for RNA release', *Journal of Virology*, 80(21), 10395.

Shim E (2010a), Chapter 2. 'Coating and laminating processes and techniques for textiles', in Smith W C (ed.) *Smart Textile Coatings and Laminates*. Cambridge, UK, Woodhead Publishing, in association with The Textile Institute, and Boca Raton, FL, CRC Press.

Shim E (2010b), 'Surface engineering of nonwoven fabric, *Advanced Textiles Conference*, 26–27 October, 2010 Orlando, FL, USA.

Shishoo R (2002), 'Recent developments in materials for use in protective clothing', *International Journal of Clothing Science and Technology*, 14(3/4), 201–215.

Singh R P and Desai S M (2004), 'Surface modification of polyethylene', *Long-term Properties of Polyolefins*,169, 231–293.

Spagnola J C (2010), *Atomic Layer Deposition on Fiber-Forming Polymers and Nonwoven Fiber Structures*. PhD Thesis. Raleigh, NC: North Carolina State University.

Sun T, Wang G, Feng, L, Liu B, Ma Y, Jiang L, and Zhu D (2004), 'Reversible switching between superhydrophilicity and superhydrophobicity', *Angewandte Chemie International Edition*, 43(3), 357–360.

Sundaram J, Choi I S, Lahann J, Tran T-N, Hoffer S, Somorjai G A, Mitragotri S, Langer R, and Kaido H (2003), 'A reversibly switching surface', *Science*, 299(5605), 371–374.

Tao X (2001), *Smart Fibres, Fabrics and Clothing*, Boca Raton, FL, CRC Press and Cambridge, UK, Woodhead Publishing.

Textor T and Mahltig B (2010), 'A sol–gel based surface treatment for preparation of water repellent antistatic textiles'. *Applied Surface Science*, 256(6), 1668–1674.

Tsujii Y, Ohno K, Yamamoto S, Goto A, and Fukuda T (2006), 'Structure and properties of high-density polymer brushes prepared by surface-initiated living radical polymerization', *Surface-initiated Polymerization I*, 197, 1–45.

Waelde L R. (2001), Chapter 79. 'Thermoset powder coatings.' in Satas D and Tracton A A, *Coatings Technology Handbook*, New York, Marcel Dekker, Inc., 691–705.

Wang L, Wang X, and Lin T (2010), Chapter 6. 'Conductive coatings for textiles', in Smith W C (ed.) *Smart Textile Coatings and Laminates*. Cambridge, UK, Woodhead Publishing in association with The Textile Institute, and Boca Raton, FL, CRC Press.

Wei Q (2009), *Surface Modification of Textiles*, Boca Raton: CRC Press; and Cambridge, UK, Woodhead Publishing, in association with The Textile Institute.

Whiteman R (1993) 'On-line gauging, control and benefits for the coating/laminating process', *Journal of Coated Fabrics*, 23, 87–104.

Wicks Z W, Jones F N, and Pappas S P (1999), *Organic Coatings: Science and Technology*, New York, John Wiley & Sons, Inc.

Williamson J E (2010), 'Textile segment weaves in infection control, innovation and savings', *Healthcare Purchasing News*, 34(9), 32.

Wu X, Zheng L, Lou Z, and Wu D (2004), 'Superhydrophobicity from microstructured surface', *Chinese Science Bulletin*, 49(17), 1779–1787.

Xu Z-K (2009), *Surface Engineering of Polymer Membranes*, New York, Springer.

Yamanaka J, Kayasuga T, Ito M, Yokoyama H, and Ishizone T (2011), 'Synthesis of water-soluble polyoligo(ethylene glycol) methacrylates by living anionic polymerization of oligo(ethylene glycol) vinyl ether methacrylates', *Polymer Chemistry*, 2(8), 1837.

Yang Q, Yu L, Wang Y, and Wei Q (2007), 'Functionalization of textile materials by plasma enhanced modification', *Journal of Industrial Textiles*, 36(4), 301–309.

Yeom B Y, Shim E, and Pourdeyhimi B (2010), 'Boehmite nanoparticles incorporated electrospun nylon-6 nanofiber web for new electret filter media', *Macromolecular Research*, 18(9), 884–890.

Young T (1805), ' An essay on the cohesion of fluids', *Philosophical Transactions of the Royal Society of London*, 95, 65–87.

Zhang J and Han Y (2010), 'Active and responsive polymer surfaces', *Chemical Society Reviews*, 39(2), 676.

Zhao B and Brittain W J (2000), 'Synthesis, characterization, and properties of tethered polystyrene-b-polyacrylate brushes on flat silicate substrates', *Macromolecules*, 33(23), 8813–8820.

Zickler D (1978), 'Coating industrial fabrics by means of the melt roll process', *Journal of Coated Fabrics*, 8, 121.

4
The use of nanomaterials in smart protective clothing

S. SUNDARRAJAN, National University of Singapore, Singapore and S. RAMAKRISHNA, National University of Singapore and Institute of Materials Research and Engineering, Singapore

Abstract: Conventional materials used in protective clothing and textile applications are discussed as well as the replacement of activated carbon in protective clothing by nanoparticles, in conjunction with nanofibers. Metal oxide nanoparticles, such as MgO, Al_2O_3, Fe_2O_3, ZnO, and TiO_2, have been shown to degrade chemical and biological warfare agents (CWA) into non-toxic products. They also enhance various properties such as mechanical properties, resistance to chemicals, flame retardancy, and antibacterial and self-cleaning properties. Finally, the application of conducting polymers in smart textiles to provide sensing and actuating properties is discussed.

Key words: protective clothing, metal oxide nanoparticles, chemical and biological warfare agents.

4.1 Introduction

Existing state-of-the-art protective clothes for chemical and biological protection use activated charcoal impregnated with metal ions, which physically adsorb most chemical warfare agents (CWA) (such as nerve and blister agents) and filter biological warfare agents (BWA) on the clothing surfaces. However, they are associated with some disadvantages, such as moisture absorption, which causes wearer discomfort, and the fact that adsorption decreases with time. Metal oxide nanoparticles have been recently studied in various applications due to their enhanced catalytic, disinfection and sensing capabilities, photoprotection capability, flame retardancy, stain resistance and self-cleaning properties. Nanofiber membranes are easy to prepare, possess high surface-area-to-volume ratio and fine, tunable pore sizes. Various nanoparticles, used in conjunction with nanofibers, their mode of incorporation and some of the issues arising in integration and their applications in protective clothing, as well as sensors studied in our laboratory and other laboratories, are presented in this chapter. Recent development of nanotechnology-enabled smart textiles with sensing and actuating properties is discussed in Section 4.6.

(a) (b)

4.1 (a) Impermeable protective clothing; (b) permeable protective clothing.

4.2 Conventional materials used in protective clothing

Filters based on glass fibers and activated charcoal are currently used in air filtration applications, such as in hospitals, protective clothing, face masks, cleanroom ventilation and cabin air cleaning. In the case of military applications, two types of suits, namely impermeable and permeable protective suits, have been widely used by soldiers to protect against nuclear, biological and chemical (NBC) contaminants (Fig. 4.1).

Permeable suits are usually worn as an overgarment, which has an outer shell fabric, an adsorbent layer, and an inner layer. The outer shell fabric is designed in such a way that it repels liquids and solid toxic materials. The adsorbent layer consists of activated charcoal impregnated with metal oxides, such as Ag, Cu, Zn, and Mo, in the presence of triethylene diamine (TEDA). The presence of TEDA removes the blood agent (cyanogen chloride) by hydrolysis and forms HCl and HCN, which are subsequently removed by Cu and Zn oxides. The arsines are removed by Cu and Ag ions. The inner layer is designed to prevent the adsorbent layer from scratching the wearer.

The impermeable protective garments are impermeable to air and are normally equipped with self-contained breathing apparatus (SCBA). Although impermeable clothing removes bacterial contaminants and particulate matter (Morrison, 2002), they are heavy, have no moisture exchange,

elevate heat stress, and are not able to protect against warfare agents. Though, lighter weight protective clothing is available, their protection duration is greatly reduced.

Air-permeable, carbon-based clothing that is designed to be worn over a uniform, for military use, is lightweight and does not require any self-contained breathing apparatus. Two types of such flexible garments that are worn by US military for protection against chemical and biological attack are the BattleDress Over-garment (BDO) and Joint Service Lightweight Integrated Suit Technology (JSLIST) (Schreuder Gibson, *et al.* 2003). However, these garments are heavy due to the added weight of carbon (2.6–3 kg).

Although, such activated charcoal-based material is very effective in removing chemical contaminants, it does not neutralize all chemical contaminants. The mechanism of contaminant removal is physical adsorption for nerve and vesicant agents. Blood and choking agents are removed by chemical reaction through the metal ions adsorbed on the activated charcoal surfaces. Some of the drawbacks associated with existing protective clothing are heavy weight, low moisture adsorption, and difficulties in disposal after use. Hence, in order to overcome these drawbacks, various new research directions are currently focused in several laboratories (especially in the US army) and in our laboratories at NUS. Recent developments in this area are highlighted in the following sections.

4.3 Use of nanoparticles in protective clothing

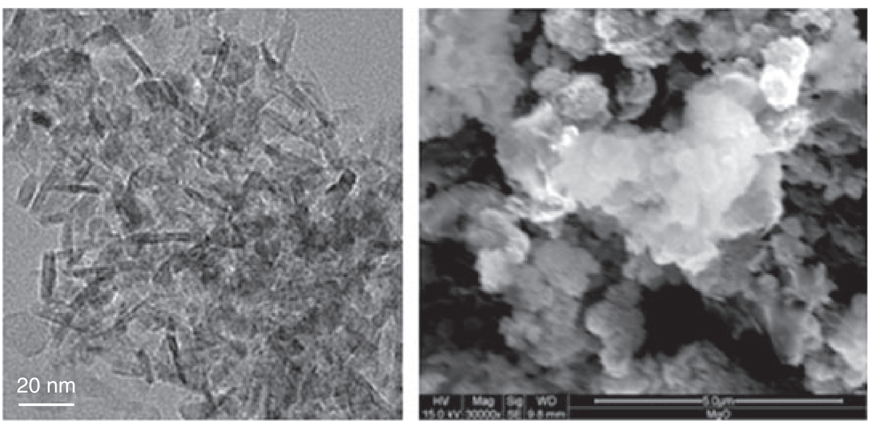
Nanoparticles possess some unique features, such as excellent magnetic, optical, surface chemistry and mechanical properties, and higher melting points; hence, they are being explored for many applications. Among them, the unique catalytic behaviour shown by metal oxide nanoparticles against CBW agents is discussed here. Metal oxide nanoparticles include MgO, Al_2O_3, Fe_2O_3, ZnO, and TiO_2.

Various methods of nanoparticle synthesis such as the cryosol technique, sol–gel method, sonochemical preparation, sonohydrolysis, high-energy ball milling, radio frequency reactive sputtering deposition, gas phase condensation, hydrothermal and precipitation method, microwave-assisted synthesis, and aerogel technique have been reported. Of these, the aerosol method has been widely used to produce a variety of metal oxides for catalytic applications due to its ability to produce high surface area materials with high reactivity.

As an example, a recent study (Sundarrajan and Ramakrishna, 2007), has reported the preparation of nanocrystalline MgO from $Mg(OH)_2$ samples, using a modified procedure, previously described by Utamapanya, *et al.* (1991). In this method of preparation, water was added, while stirring, to a

magnesium methoxide solution in a toluene/methanol mixture. After overnight stirring, the gel was transferred into an autoclave heated from room temperature to 250 °C at a 1 °C/min heating rate and kept at this temperature for 15 min. After solvent removal, a white powder was obtained. The white powder was then heated from room temperature to 220 °C at 1 °C/min, and kept at 220 °C for 5 h; and heated from 220 °C to 400 °C at 1 °C/min and kept at this temperature for 4 h. The surface area of the MgO nanoparticles so synthesized is found to be 155 m^2/g by the Brunauer–Emmett–Teller (BET) method, which is lower than the value reported in the literature (400 m^2/g) (Utamapanya, 1991). Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the synthesized nanoparticle are shown in Figs 2a and 2b. The nanoparticles have a diameter of 2.7–3.3 nm and length of 9–14 nm.

Metal oxide nanoparticles such as MgO, TiO_2, Al_2O_3 and other oxides have been shown to degrade chemical and biological warfare agents (CWA). Metal oxides in nanoform exhibit high catalytic performance as compared to the same material prepared by conventional methods (Rajagopalan *et al.*, 2002). This enhanced activity is not only due to their high surface area, but also because of other factors such as their small crystal size, high porosity, irregular shape and surface defects such as anion and cation vacancies (Morris and Klabunde, 1983). In these oxides, the mechanism of degradation of the chemical warfare agent is found to be destructive adsorption,



(a) (b)

4.2 (a) TEM image and (b) SEM image of MgO nanoparticles. (Reproduced with permission from Sundarrajan S and Ramakrishna S, 'Fabrication of nanocomposite membranes from nanofibers and nanoparticles for protection against chemical warfare simulants, *J. Mater. Sci.*, 2007, 42, 8400–07 Springer, DOI: 10.1007/s10853-007-1786-4).

whereas in conventional activated charcoal, physisorption is the mechanism for contaminants removal. Moreover, the amount of paraoxon (a nerve agent simulant) adsorption on the nano form is much higher than on activated charcoal (Rajagopalan *et al*., 2002).

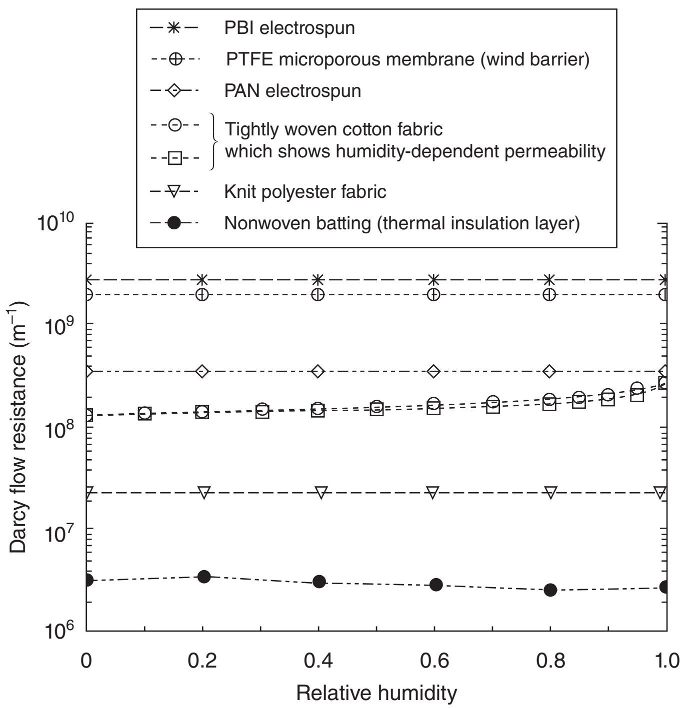
The mode of binding of nanoform samples differs from conventional bulk samples. In nanoform samples, the mode of binding with CO_2 is found to be unidentate and is in a bridging type fashion (AP–CaO, AP–MgO), whereas bidentate coordination is mostly found in conventionally prepared samples (Koper *et al*., 1997). This is because there are small crystallites having a high ratio of edge/surface ions present in nano samples, whereas conventionally prepared samples have more flat planes. It is difficult to characterize nanosamples of metal oxide particles (such as MgO and CaO) by high-resolution TEM images due to their comparatively low electron densities and their insulator properties when compared with conventionally prepared samples.

4.4 Use of electrospun nanofibers and nanoparticles in protective clothing

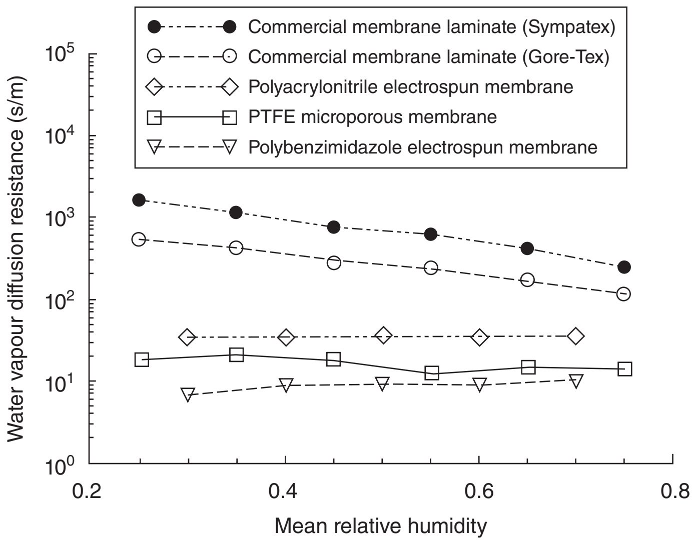
Electrospun nanofibrous materials (ENM) are currently being explored as a means of replacing granular materials such as charcoal because the fraction of ENM required is lower. The electrospinning process to produce nanofibers is perhaps the most promising of all nanotechnologies, in terms of versatility and cost. During electrospinning, a polymer solution is forced through a spinneret under the influence of a high electric voltage (15 to 30 kV). The resultant liquid jet then passes through a controlled temperature and humidity environment where the solvent evaporates before deposition of fiber on the collector. Charges created on the jet surface repel each other and create a multijet. When the applied voltage is higher than the surface tension of the polymer solution, the jet is ejected from the surface and deposited on the collector. The deposition rate of nanofibers varies from 2 m/sec to 200 m/sec, depending on the solution physical properties and processing conditions.

Careful selection of polymers and spinning parameters enables the achievement of unique, finely-tuned fabric properties, such as strength, porosity, pore size distribution, and weight. One of the salient features of nanofibers is that the pores present in the nanofibers provide excellent resistance to the penetration of aerosolized chemical warfare agents and selectively allow a significant amount of water vapour to transport through them. This is highly desirable when these nanofibers are used in a protective fabric application because then evaporative cooling of the body becomes possible.

Gibson *et al*. (1999) have studied the water vapour diffusion and gas convection properties of electrospun nanofibers using a dynamic moisture permeation cell. They observed that transport of water vapour proceeded by pure diffusion, driven by differences in vapour concentration in the absence of pressure difference across the sample, whereas transport of gas and vapour proceeds through convective transport when a pressure difference exists in the sample. It has been observed that the convective gas flow resistance of nanofibers is much higher than that of woven fabrics i.e. clothing materials (Fig. 4.3). The magnitude of convective flow resistance for a hydrophobic polymer such as polybenzimidazole, is greater when compared with a hydrophilic fiber such as polyacrylonitrile, as shown in Fig. 4.3. However, resistance to water vapour diffusion is lower for electrospun membranes when compared with commercially available laminates (Fig. 4.4) (Gibson *et al*., 1999). This is highly desirable when these nanofibrous materials are applied to protective clothing applications, which require materials with high rates of water vapour diffusion and low air permeability.



4.3 High convective gas flow resistance of microporous membranes and electrospun nonwovens. (Reproduced with permission from Gibson P W, Schreuder-Gibson H L, and Rivin D (1999), 'Electrospun fiber mats: transport properties', *AIChE J.*, 45(1), 190–195, John Wiley and Son Limited, DOI: 10.1002/aic.690450116). PBI, poly(benzimidazole); PTFE, poly(tetrafluoroethylene); PAN, polyacrylonitrile.



4.4 Excellent water vapour transport properties of electrospun nonwovens. (Reproduced with permission from Gibson P W, Schreuder-Gibson H L, and Rivin D (1999), 'Electrospun fiber mats: transport properties', *AIChE J.*, 45(1), 190–195, John Wiley and Son limited, DOI: 10.1002/aic.690450116).

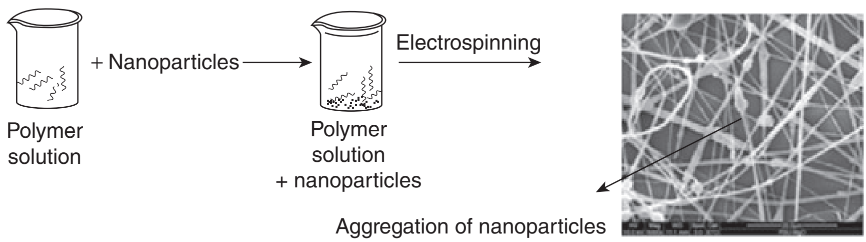
It has also been reported that the air flow resistance of electrospun nanofibers increases with increase in the coating layer and is comparable to a microporous PTFE membrane (Schreuder-Gibson *et al.*, 2002).

Reactive additives such as (3-carboxy-4-iodosobenzyl) oxy-b-cyclodextrin have been incorporated into nanofibers, and these hydrolyse an organophosphorus nerve agent 11.5 times faster than activated charcoal (Ramakrishna *et al.*, 2006). This enhanced catalytic activity is attributed to the high surface area of the nanofibers, which allows faster diffusion of nerve agents into the nanofiber. Silver nanoparticles have also been incorporated into nanofibers of cellulose acetate (CA) by electrospinning a mixture of $AgNO_3$ and polymer solutions (Lala *et al.*, 2007). These nanofibers kill gram-negative bacteria, namely *E. coli* and *P. aeruginosa*, and hence they can be potentially applied as filters for protection against bacterial contamination.

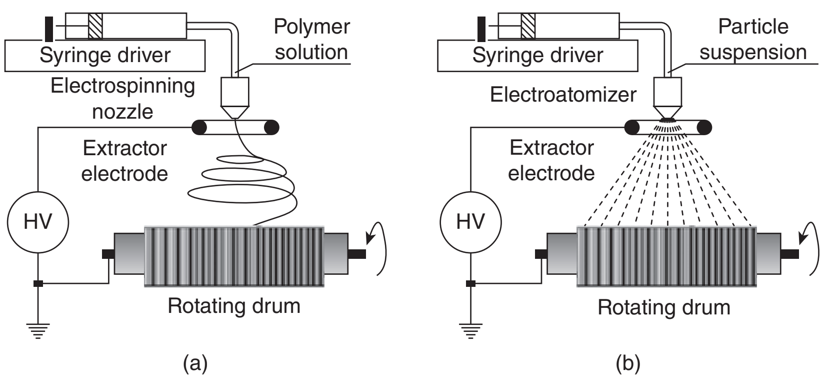
Although various individual metal oxides, binary metal oxides, and supported metal oxides are reported in the literature, their usage in nanoparticle form is difficult due to aggregation and containment when intended for clothing and other applications. Electrospun nanofibers are the best materials to support these catalysts for such applications. Hence, nanoparticles were mixed with polymer solution and subsequently electrospun by Sundarrajan and Ramakrishna (2010a). The percentage of nanoparticles

incorporation into nanofibers was found to be 35% of the total solid content of the fiber, above which the solution was not spinnable. This is because of the reduction of polymer concentration in solution to form the required Taylor cone. The obtained nanocomposite membranes decontaminated a simulant of a nerve gas, paraoxon. However, the amount of nanoparticles that are available on the surface was lower and most of them were covered by polymer material (Fig. 4.5) and thereby they are not fully available on the surface for catalytic applications (Sundarrajan and Ramakrishna, 2010b). This problem was overcome by the combination of electrospinning technique with electrospraying technique, as shown in Fig. 4.6.

The working principle and salient features of the electrospinning process are discussed elsewhere in the chapter. In the case of the electrospraying technique, comparatively low voltages and low viscosity solutions are used when compared with the electrospinning process. In the electrospraying technique, the electric charge draws the low viscosity solution in the form of a fine jet, which eventually breaks up into small droplets or particles (Jaworek and Krupa, 1999). Electrospray has been used to deposit ultra-thin films of inorganic, organic and biological materials, to generate



4.5 Conventional method of preparing nanofibers with nanoparticles.

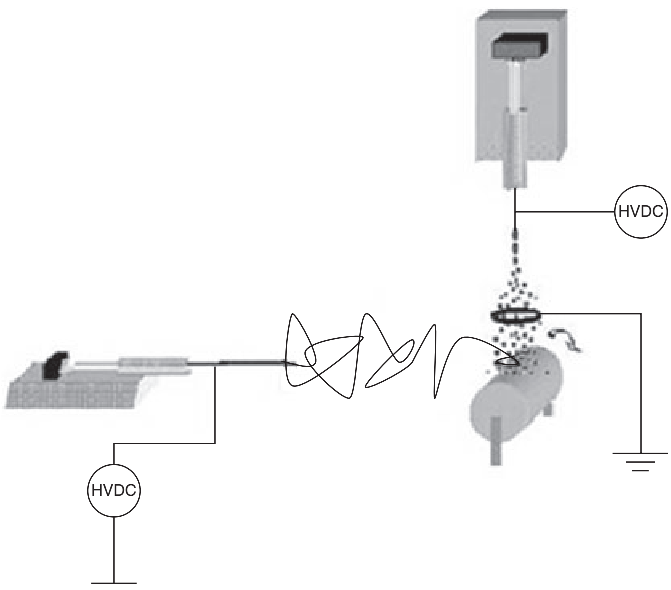


4.6 Schematic diagram of layer-by-layer deposition of nanofibers and nanoparticles. (a) Electrospinning of polymer first. (b) Electrospraying of nanoparticles. HV, high voltage.

nanoparticles and quantum dots, to sort them according to their sizes, and to help with dispersion and delivery of nanomaterials. This technique has been commercially applied in various fields such as mass spectrometry, painting, and inkjet printing.

The importance of the electrospraying technique was realized by its inventor, John B. Fenn, in winning the Nobel Prize for Chemistry in 2002 (Fenn, 2003). By using this technique, he achieved the vaporization of large biomolecules into a gaseous phase without decomposition, which, in conjunction with mass spectrometry (ESIMS), has been used in the laboratory to identify the large molar mass of proteins, synthetic polymers, end groups of polymers and sequence distribution of polymer chains, etc.

With this in mind, a combination of electrospraying with electrospinning technique was investigated, which could also solve the existing problems in large area use of nanomaterials in catalysis, defense, and biological applications. Two modes of combinations investigated are presented in Figs 4.6 and 4.7. The layer-by-layer nanocomposite membranes (LBL membranes) were fabricated by the *consecutive* electrospraying of a nanoparticle



4.7 Schematic diagram of simultaneous electrospinning and electrospraying technique. (Reproduced with permission from M. Roso, S. Sundarrajan, D. Pliszka, S. Ramakrishna, and M. Modesti, 'Multifunctional membranes based on spinning technologies: the synergy of nanofibers and nanoparticles', *Nanotechnology*, 2008, 19, 285707, IOP Publishing Limited, DOI: http://dx.doi.org/10.1088/0957-4484/19/28/285707). HVDC, high voltage direct current.

suspension (in the presence of a surface modifier, MEMO) after electrospinning a polymer solution. Simultaneous nanocomposite membranes (SIM membranes) were fabricated by the *simultaneous* electrospinning of a polymer solution and electrospraying of a nanoparticle suspension from two separate capillary nozzles (Roso *et al.*, 2008). The nanocomposite membranes' ability to detoxify a warfare agent was tested by using a nerve agent stimulant, paraoxon. The activity of the SIM membranes and LBL membranes were found to be 52% and 48%, respectively, when compared to the nanoparticles. This activity is slightly higher than conventional mixing of nanoparticles with polymer (activity of 35%). The percentage decomposition efficiency of these nanocomposite membranes when compared with nanoparticles was calculated by the following formula, using UV spectroscopy:

$$[A_s - A_c] - [A_s - A_{con}]/[A_s - A_{NP}] \tag{4.1}$$

where A_s is absorbance observed for the stock solution, A_c is absorbance observed for the nanocomposite membrane, A_{con} is absorbance observed for the polysulfone polymer membrane, and A_{NP} is absorbance observed for the nanoparticles. When the pressure drop test was conducted, the pressure drop increased by 19% for the SIM membranes as compared with the pure nanofibrous membrane, whereas for the LBL membranes, the pressure drop decreased, mainly as a function of the raised nanoparticle content (Roso *et al.*, 2008). This study suggests that the LBL membranes, with decreased flow resistance and improved performance, can potentially be used as air-con filters (in hospitals, industry, airplanes, etc.) and in protective clothing applications.

4.5 Applications of nanoparticles in protective textiles

The growth of microorganisms on conventional clothing takes place due to various environmental and textile factors, which include temperature, presence of dust, humidity, soil, spilled food, sweat and oil secretions, and the finishing materials on the textile surfaces. These microorganisms in clothing cause undesirable effects such as discoloration, staining, deterioration of fibers, unpleasant odour and potential health hazards (Sundarrajan *et al.*, 2010b). Cyclodextrin (CD) exists in three forms: i.e. α, β, and γ forms. Among them, β-CD can be chemically bonded to cellulosic fibers to control odour. The β-CD molecules act as host molecules, as they have non-polar cavities that can incorporate bad smelling guest molecules. The guest molecules are removed by washing.

Nanoparticles have also been used in the development of high-performance swimwear; this application has been developed following studies on the skin of sharks. The shape and positioning of riblets varies

across shark skin to provide minimized flow resistance and thereby the shark slides through the water. Nanoparticles were self-assembled, like dermal denticles on shark skin. Such a design has been used for the fabrication of swim suits that were utilized in recent Olympic competitions. Lower friction coefficients on the fabric reduce the flow resistance. Nanomaterials are currently being incorporated into textile fabrics to enhance the mechanical properties and coloration, improve resistance to chemicals, to provide flame retardant and antibacterial properties, and to provide self-cleaning action.

4.5.1 Enhanced UV protection and antimicrobial properties

Two of the most widely used metal oxides for UV protection in textiles are TiO_2 and ZnO, both of which have the ability to absorb UV radiation (Becheri *et al.*, 2007). Nano-TiO_2 and modified nano-TiO_2 with aminosilane, applied to textiles, show high absorption of UV radiation in a full wavelength range and enhanced photocatalytic properties have also been reported (Sojka-Ledakowicz *et al.*, 2009). Biocidal cotton bandages coated with CuO nanoparticles by the sonochemical method have demonstrated good biocidal properties and the nanoparticles were stable to at least 20 washings (Abramov *et al.*, 2009).

A combination of silver and TiO_2 gives a synergistic effect and hence synthesis of Ag on TiO_2 surfaces was undertaken. Ag/TiO_2 and Pd/TiO_2 sols were coated onto viscose fabrics by the solvothermal method, and their photocatalytic and antimicrobial properties were measured (Mahltig *et al.*, 2007). Similarly, Ag with TiO_2 was deposited on activated cotton and polyester, and cured at a specific temperature to activate the bactericidal properties and to improve the bonding capacity of nanoparticles with textiles (Kiwi, 2010). However, a red shift peak was observed in UV-Visible measurement due to electron exchange between Ag and TiO_2 and this led to the appearance of a brownish color on the textile, which would limit the application.

4.5.2 Enhanced mechanical strength and flame resistance

A nanocomposite fiber prepared from nylon with clay nanoparticles showed flame retardant, UV protection and anticorrosive behaviours. The fiber, after the incorporation of 5% clay, exhibited 40% higher tensile strength, 60% higher tensile modulus and 60% higher flexural strength, and the heat distortion temperature increased from 65 °C to 152 °C (NIST website, Cornell University website).

A coating of monazite has been applied to thermal-protection blankets to increase the service temperature for re-entry spacecraft (Davis *et al.*, 1999). SiO_2 nanoparticles with crosslinking compounds exhibit excellent

mechanical properties, such as scratch resistance, anti-adhesive and anti-static properties. They also exhibit excellent UV protection and IR absorption properties.

4.5.3 Improved electrical and coloration properties

The electrical conductivity of electrospun nanofibers such as PAN, poly(methyl methacrylate), and PAN/poly(acrylonitrile-co-styrene) fibers has been found to improve when single-walled carbon nanotubes (SWCNT) were incorporated into nanofibers (Liu *et al*., 2005). Polypropylene fiber is not dyeable by itself, due to the absence of dye sites. When nanoclay has been added, polypropylene fiber can be dyed with good dye levelness. This is due to the high distribution uniformity of the clay, resulting from its high surface area. (Fan *et al*., 2003; Mani, 2003).

Dispersions of carbon black nanoparticles at 5% and 10% concentrations, in the presence of dispersing agents, were padded onto PET and acrylic fabrics. Greater shade depth was obtained when the diameter of the nanoparticle was 8 nm (Li and Sun, 2003). Most of the toxic chemicals and dyestuffs used to colour the textiles are hazardous to the environment, and, in particular, discharge water causes environmental pollution. Cleaner production of textiles using eco-friendly dyes by greener technology may have to be achieved in future.

4.5.4 Self-cleaning and stain-repellent properties

Thin film coatings of TiO_2 on cotton to give self-cleaning (lotus leaf effect) textiles have been explored by Daoud and Xin (2004). TiO_2 in pure anatase form was coated on textiles at 97 °C by boiling in water for 3 h. Titania can be used as a self-cleaning antibacterial photocatalyst for the decomposition of organic dirt, environmental pollutants, and harmful microorganisms (Daoud and Xin, 2004; Kiwi and Pulgarin, 2010).

Recently, the development of bioinspired super-hydrophobic surfaces to achieve self-cleaning properties has been studied by various groups (Deng *et al*., 2010; Liu *et al*., 2009; Chen *et al*. 2011). Development of a fabric containing a tailored hydrophobicity/hydrophilicity concept combination was also studied, wherein the hydrophilicity feature is important to provide garment comfort, and the hydrophobicity to provide self-cleaning and stain repellency.

4.5.5 Multifunctional textiles

To overcome issues such as discoloration, staining and poor stability on fabric surfaces, various concentrations of a cross-linkable polysiloxane

(XPS) and Ag mixed with XPS on TiO_2 treated fabrics have been investigated (Dastjerdia *et al.*, 2010). Some of the advantages of XPS include stabilization of nano particles on fabric surfaces; compensation for some adverse effects of inorganic nanoparticles such as decreased conductivity and softness; and increased abrasion resistance of nanoparticles on the garment surfaces. It also prevents direct contact of nanoparticles with the human body and possible inhalation of nanoparticles during manufacturing. Some of the characteristics of XPS, Ag and TiO_2 treated fabrics, such as hydrophilicity, antibacterial efficiency, anti-staining properties, stain photo degradability, UV protection, air permeability and washing durability have been evaluated (Dastjerdia *et al.*, 2010). This concept may provide sufficient thermal stability for autoclaving when it is explored for medical textile applications in future.

4.6 Smart textiles using nanoparticles

In the previous sections, materials developed for protection against toxic vapours and textiles with self-cleaning and antibacterial properties were presented. Recently, due to the rapidly changing needs of consumers, next generation materials are being developed and integrated with textiles called 'smart textiles'. Smart textiles can monitor the health status of a person, such as temperature, movement, chemicals, heart rate, respiration, mechanical parameters and many more. They are classified into two categories: passive and active smart textiles. *Passive smart textiles* are capable of sensing environmental conditions and stimuli from mechanical, thermal, chemical, electrical or magnetic sources, whereas *active smart textiles* possess both sensors and actuators, such as regulating ability to maintain the wearer's body temperature.

The basic components required for smart textiles are sensors, actuators and electronics (communications, computing, and monitoring) units. In the initial stage of development, these units are overlaid on textiles by conventional electronics. Recently, nanotechnology has enabled integration, and potential applications are being explored in smart textiles. Some of the materials that are applied for smart textiles developments include conducting polymers (CPs), carbon nanotubes (CNT) and piezoelectric materials. The incorporation of these materials enables additional functionalities, such as sensing, actuating, and communicaton. Some of the applications include sports, healthcare, military and the fashion industry.

4.6.1 Conducting polymers in sensing applications

Conducting polymers are extensively applied in sensing and actuator applications. Nanofibers have a unique property in that they show enhanced

sensitivity and selectivity when compared with the same material in bulk form, due to their high active area and ease of charge transfer. Metal oxides such as zinc oxide have been extensively studied because of their high chemical stability, low cost, good flexibility in fabrication, and known sensitivity towards gases such as NH_3, O_3, NO_2, CO, H_2, and other analytes (Wang *et al.*, 2004).

Conducting polymers in nanofibrous form are unique materials that show faster response when compared with their bulk form. The response time of polyaniline nanofibers towards gaseous analytes such as ammonia was found to be less than 4 s (MacDiarmid, 2001). Sensors for detection of warfare agents have been developed, although these have yet to be incorporated into electrospun nanofibers or textiles (Campanell *et al.*, 1996). Recently, a non-woven organic solar cloth made of P3HT/PCBM blend (poly(3-hexyl thiophene)/[6, 6]-phenyl-C61-butyric acid methyl ester), made by core–shell electrospinning technique for energy harvesting applications has been reported (Sundarrajan *et al.*, 2010c). Although the efficiency of the solar cells is very low, this can be integrated with protective clothing and textile applications, which will have both sensing and energy harvesting capability to charge hand-held mobile electronics such as mobile phones, PDAs and many more.

4.6.2 Conducting polymers as artificial muscles in actuator applications

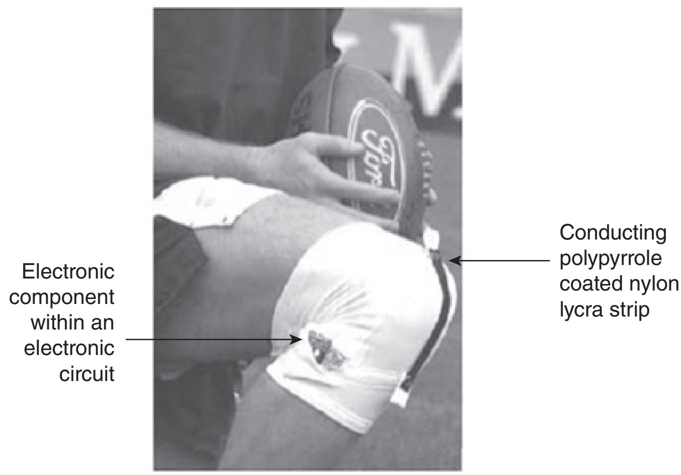
Rapid response rates in natural muscles are dependent upon the utilization of microscopic actuator elements (myosin and actin). The work-step of the smallest individual muscle actuator is provided by the swivel-like motion of the pear-shaped head of a myosin molecule (which is about 190 A° long and 50 A° wide) that moves a thin actin fiber along the length of a thick myosin fiber (Bowman, 1996). This actuator work-step displaces the thick fiber relative to the thin muscle fiber by about 50 to 100 A°, and generates a force of roughly 5 pN. Several hundred such myosin molecules in a thick fiber give such chain-end actuators that act to increase the overlap between thick fibers and thin fibers, thereby providing the muscle contraction (Bowman, 1996).

Conducting polymers belong to a broad class of electrically actuated polymeric materials known as electroactive polymers (EAPs). They are classified into two groups – ionic and electronic EAPs. Ionic polymer metal composites and conjugated polymers are grouped into ionic EAPs and volume changes in these materials are dependent on ion and solvent transport: they are suitable for operation in a biofluid environment. Some of the electronic EAPs are piezoelectric polymers, electrostrictive and dielectric elastomers. They require high voltages and are usually shielded from a

fluid environment. The basics of conducting polymers and their surface modification, as well as their biomedical applications, can be found elsewhere in a recent review article (Ravichandiran *et al.*, 2010).

The actuation property of ionic EAPs arises from their volume changes. When a potential is applied to an EAP, addition or removal of charge from the polymer backbone takes place, and to balance the charge a flux of ions takes place. The insertion of ions between polymer chains results in switching of the polymer chain's dimensions between fully expanded and contracted states. Conformational changes of the polymer backbone also take place. EAPs possess high Young's modulus (ca.1 GPa) and high tensile strength (>100 MPa), combined with low voltages (2 V), making them attractive for many applications.

Conventional strain gauges for movement measurement in mechanical sensors can be replaced by flexible electroactive EAP-coated textile fabrics. The presence of EAPs can provide piezoresistive properties in coated materials and may enable the detection of local strain on a fabric. Conducting polypyrrole coated on nylon and Lycra textiles has been prepared by an *in situ* chemical polymerization process, and a strip of these materials has been used as a knee sleeve for sports training (Fig. 4.8). When the coated fabric is stretched, changes in resistance of the textile results and thereby different sounds will be emitted from the textiles, depending on the strain (Wu *et al.*, 2005, Fig. 4.8). This concept can be applied for injury prevention, rehabilitation, and medical treatment in future. Textile fibers of EAPs such as polyaniline are processed by wet spinning techniques (Bowman *et al.*, 2005). The DC conductivities for unstretched and stretched fibers are 72 and



4.8 The knee sleeve. (Courtesy of CSIRO Textile and Fiber Technology.)

725 Ω^{-1} cm^{-1}, respectively. They can be formed into yarns and other fabric structures.

EAP-based mechanical actuators can attain average stresses 10 to 20 times more than those produced from natural muscle (Della Santa *et al.*, 1997), realize strains >20% compared with natural muscle (Hara *et al.*, 2004), and achieve a fast freestanding beam actuation frequency of 40 Hz (Wu *et al.*, 2006). EAP-based actuators show muscle-like behavior; this can be potentially used in various applications such as swimming device/robotic fish. Recently, electrochemical actuators based on 1-butyl-3-methyl imidazolium tetrafluoroborate as an ionic liquid with polyaniline nanofibers were developed and the actuators showed an excellent life-time of over one million redox cycles (Lu and Mattes, 2005). Other actuator materials such as piezoelectric materials (quartz, lead zirconate (PZT)) have less strain and require higher voltages for actuation (hundreds of volts).

To date, integration of health-monitoring tools into textiles has been focused mainly on physiological measurements (body temperature, electrocardiogram, electromyogram, breath rhythm, etc.) by remote monitoring for applications targeting sport performance and detection of illness. A new area of research of interest to the Biotex company is in biochemical measurements of body fluids via sensors distributed on a textile substrate. Biotex is addressing the sensing part and its electrical or optical connection to a signal processor. The researchers are aiming to develop sensing patches, adapted to different targeted body fluids and biological species to be monitored, where the textile itself is the sensor. The extension to the whole garment and integration with physiological monitors is part of the roadmap of the consortium (Biotex, website).

4.7 Chameleon fibers

Materials that change colour (due to change in optical properties) in response to an applied electric field or magnetic field are known as chameleon materials. Among the various approaches studied, electrochromism and electroluminescence are two widely used approaches for achieving colour change. Various organic (viologens), inorganic (Ir_2O_3, WO_3) and polymeric materials (polypyrrole, polythiophene, polyaniline, polycarbazole) show excellent electrochromic properties. These materials exhibit a reversible and visible change in absorbance or reflectance behaviour when electrochemical oxidation or reduction reactions, occur, and this phenomenon is known as electrochromism. Some conducting polymers show good colour contrast and long cycle lifetimes, in addition to nonlinear optical applications and smart windows. Desirable properties required for electrochromics are fast and reversible switching between oxidation and reduction (redox) states.

In the case of electroluminescence, a fluorescent material emits light when electrically excited as the molecule in the excited state returns to the ground state. In such materials, a high efficiency emitter is highly desirable. Although the development of fiber and fabric substrates for chameleon fibers is in progress, a simple process can be used to polymerize conducting monomers on the surface of textiles (Gregory *et al*., 1989). Reynolds and co-workers at the University of Florida (USA) have been successful in the development of electrochromic materials with tailored colours. Friend and co-workers at the University of Cambridge have synthesized polymers as emissive layers with good light-emitting diode (LED) applications. Gregory and co-workers are exploring these chameleon fibers based on the concept of a core electrode coated by emissive conducting polymers, over which a transparent electrode is formed. (Gregory, website). Recently, electrochromic composites based on carbon nanotube and poly (diacetylene) fibers have been synthesized by directly coating diacetylenic precursors onto nanotubes, followed by topochemical polymerization of diacetylenic moieties under UV light (Peng *et al*., 2009).

4.8 Conclusion and future trends

Glass fibers and activated charcoal are currently used in air filtration applications. The charcoal-based filter, being incapable of filtering out chemical contaminants, can be replaced with polymer-based nanofibers embedded with nanoparticles. The reduced size of the pores present between nanofibers excludes aerosol particles in particular. They have excellent water and gas transport properties and provide good resistance to aerosolized chemical warfare agents.

Although water and gas transport properties of electrospun nanofibers are tested, to the best of the authors' knowledge, the transport properties of electrospun nanofibers after incorporation of reactive materials (e.g. sorbents, nanoparticles, zeolites and reactive chemicals such as β-CD-IBA complex) have not been studied so far. Studies in this area will not only shed light on the fundamental understanding of transport properties of reactive materials incorporated into fibers, but also result in new commercial applications. These will be based on improved filtration efficiency, protection duration, nonselective decontamination efficiency, and weight reduction. The market size for the nanofiber HEPA filter has been projected as over US $179 millions in 2012 and $251 millions in 2021 (Frost, website). This shows that nanofibers have a bright future in the commercial market.

Although extensive research on the coating of nanoparticles onto textiles has been carried out, the stability of nanoparticles on textile surfaces to washing is questionable, as there is no attraction between them due to difference in surface energy between their interfaces. To overcome this

problem, there are two approaches that can be adopted. The most presented method involves functionalization and various treatments such as drying, curing etc. on textile surfaces, which is time-consuming and costly. A recent approach involves the use of functionalized nanoparticles such as XPS on textile surfaces. This needs to be studied in detail in the future.

In addition to protection, the development of next generation materials based on nanotechnology-enabled smart textiles is an encouraging one. The interconnections used in conventional silicon and metal components are problematic to apply to smart textiles, making the integration of basic components such as sensors, actuators and electronics into flexible and soft textiles very challenging. However, recently developing nanotechnology-based materials will overcome those obstacles and will pave a way for a flexible and viable product. Cleaner production of textiles using eco-friendly dyes by greener technology may have to be looked into in future.

4.9 Sources of further information and advice

Interested readers are advised to read a review article by Schreuder-Gibson (2003), wherein various protective garments used by the military, different active ingredients incorporated within fibers, and detection of warfare agents are overviewed.

Various synthetic routes adopted for the preparation of catalytic active metal oxide nanoparticles are highlighted in a recent review article by the authors (Sundarrajan *et al.*, 2010b). These include TiO_2, MgO, and many more as potential catalysts for the decontamination of chemical and biological warfare agents, and their comparison with conventional samples, TiO_2 photocatalysts, and mixed metal oxides, high aspect ratio ceramic oxide nanofibers and some of the issues concerning integration of metal oxides into fabrics as sensors for use in protective clothing, wipe materials, and textiles. The basics of electrospinning of nanofibers and their potential applications in tissue engineering and protective clothing can be found in a book written by the authors (Ramakrishna, 2005). More details on the working principle of actuators based on conducting polymers can be found in a review article by Bowman (1996).

4.10 References

Abramov OV, Gedanken A, Koltypin Y, Perkas N, Perelshtein I, Joyce E, and Mason TJ (2009), 'Pilot scale sonochemical coating of nanoparticles onto textiles to produce biocidal fabrics', *Surf Coat Technol*, 204, 718–722.

Becheri A, Durr M, Nostro PL, and Baglioni P (2007), 'Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers', *J Nanoparticle Res*, 10, 679–689.

Biotex Website, http://www.biotex-eu.com (accessed November 2011).

Bowman D (1996), 'Conducting polymer artificial muscles', *Synth Met*, 78, 339–353.

Bowman D and Mattes BM (2005), 'Conductive fibre prepared from ultra-high molecular weight polyaniline for smart fabric and interactive textile applications', *Synth Met*, 154, 29–32.

Campanell L, Colapicchioni C, Favero G, Sammartino M, and Tomassetti M (1996), 'Organophosphorus pesticide (paraoxon) analysis using solid state sensors', *Sens Actuators B*, 33, 25–33.

Chen L, Han D, and Jiang L (2011), 'On improving blood compatibility: from bio-inspired to synthetic design and fabrication of biointerfacial topography at micro/nano scales', *Colloids and Surfaces B: Biointerfaces*, 85, 2–7.

Daoud WA and Xin JH (2004), 'Nucleation and growth of anatase crystallites on cotton fabrics at low temperatures', *J Am Ceram Soc*, 87 (5), 953–955.

Dastjerdia R, Montazera M, and Shahsavan S (2010), 'A novel technique for producing durable multifunctional textiles using nanocomposite coating', *Colloids and Surfaces B: Biointerfaces*, 81, 32–41.

Davis JB, Marshall DB, Oka KS, Housley RM, and Morgan PED (1999), 'Ceramic composites for thermal protection systems', *Composites Part A: Applied Science and Manufacturing*, 30A (4), 483–488.

Della Santa A, Rossi DD, and Mazzoldi A (1997), 'Characterization and modelling of a conducting polymer muscle-like linear actuator,' *Smart Mater Struct*, 6, 23–34.

Deng B, Cai R, Yu Y, Jiang H, Wang C, Li J, Li L, Yu M, Li J, Xie L, Huang Q, and Fan C (2010), 'Laundering durability of superhydrophobic cotton fabric', *Adv Mater*, 22, 5473.

Fan Q, Ugbolue SC, Wilson AR, Dar YS and Yang Y (2003), 'Nanoclay-modified polypropylene dyeable with acid and disperse dyes', *AATCC Review*, 3(6), 25–28.

Fenn JB (2003), 'Electrospray wings for molecular elephants (Nobel lecture)', *Angew Chem Intl Ed*, 42, 3871–3894.

Frost website, www.frost.com. U.S. industrial air filtration markets #N713–19 & North American HVAC air filters market #N64F-19 (accessed November 2011).

Gibson PW, Schreuder-Gibson HL, and Rivin D (1999), 'Electrospun fiber mats: transport properties', *AIChE Journal*, 45(1), 190–195.

Gregory RV, Kimbrell WC, and Kuhn HH (1989), 'Conductive textiles', *Synth Met*, 28, C823-C835.

Gregory RV, Hanks T, Samuels RJ, Dynamic color change Chameleon fiber systems, http://www.ntcresearch.org/pdf-rpts/Bref0603/M01-CL07-03e.pdf, Accessed on 8th November 2011.

Hara S, Zama T, Takashima W, Kaneto K (2004), 'Gel-like polypyrrole based artificial muscles with extremely large strain', *Polym J*, 36, 933–936.

Jaworek A and Krupa A (1999), 'Classification of the modes of EHD spraying', *J Aerosol Sci*, 30, 873–883.

Kiwi J and Pulgarin C (2010), 'Innovative self-cleaning and bactericide textiles', *Catal Today*, 151, 2–7.

Koper OB, Lagadic I, Volodin A, and Klabunde KJ (1997), 'Alkaline-earth oxide nanoparticles obtained by aerogel methods. Characterization and rationale for unexpectedly high surface chemical reactivities', *Chem Mater*, 9, 2468–2480.

Lala NL, Ramaseshan R, Bojun Li, Sundarrajan S, Barhate RS, Ying-jun L, and Ramakrishna S (2007), 'Fabrication of nanofibers with antimicrobial functionality

used as filters: protection against bacterial contaminants', *Biotechnol Bioeng*, 97, 1357–65.

Li D, and Sun G (2003), 'Coloration of polyester and acrylic fabrics with carbon black nanoparticles', *AATCCReview*, 3(12), 19–22.

Liu J, Wang T, Uchida T, and Kumar S (2005), 'Carbon nanotube core–polymer shell nanofibers', *J. Appl Polym Sci*, 96 (5), 1992–1995.

Liu M, Wang S, Wei Z, Song Y, and Jiang YL (2009), 'Bioinspired design of a superoleophobic and low adhesive water/solid interface', *Adv Mater*, 21, 665.

Lu W, and Mattes BR (2005), 'Factors influencing electrochemical actuation of polyaniline fibers in ionic liquids', *Synth Met*, 152, 53–56.

Mahltig B, Gutmann E, Meyer DC, Reibold M, Dresler B, Günther K, Faßler D, and Böttcher H (2007), 'Solvothermal preparation of metallized titania sols for photocatalytic and antimicrobial coatings', *J Mater Chem*, 17, 2367–2374.

Mani G, Fan Q, Ugbolue SC, and Eiff I (2003), 'Effect of nanoparticle size and disribution on the dyeability of polypyroylene', *AATCC Review*, 3 (1), 22–26.

Morris RM, and Klabunde KJ (1983), 'Formation of paramagnetic adsorbed molecules on thermally activated magnesium and calcium oxides: characteristics of the active surface sites', *Inorg Chem*, 22, 682.

Morrison RW (2002), Overview of current collective protection filtration technology. Presented at the 2002 *NBC Defense Collective Protection Conference*, Orlando, FL, USA, 30 October–1 November 2002.

NIST Website, http://fire.nist.gov/bfrlpubs/fire99/art164.html (accessed November 2011).

Peng H, Sun X, Cai F, Chen X, Zhu Y, Liao G, Chen D, Li Q, Lu Y, Zhu Y, and Jia Q (2009), 'Electrochromatic carbon nanotube/polydiacetylene nanocomposite fibres', *Nature Nanotechnol*, 4, 738–741.

Rajagopalan S, Koper O, Decker S, and Klabunde KJ (2002), 'Nanocrystalline metal oxides as destructive adsorbents for organophosphorus compounds at ambient temperatures', *Chem Eur J*, 8, 2602–2607. (DOI: 10.1002/1521-3765(20020603)).

Ramakrishna S (2005), *An Introduction to Electrospinning and Nanofibers*, World Scientific Publishing, Singapore, 117.

Ramakrishnan R, Sundarrajan S, Yingjun L, Barhate RS, Lala NL, and Ramakrishna S (2006) 'Functionalized polymer nanofibre membranes for protection from chemical warfare stimulants', *Nanotechnology*, 17, 2947–2953.

Ravichandran R, Sundarrajan S, Venugopal JR, Mukherjee S, and Ramakrishna S (2010), 'Applications of conducting polymers and their issues in biomedical engineering', *J. R. Soc. Interface*, 7, S559–S579.

Roso M, Sundarrajan S, Pliszka D, Ramakrishna S, and Modesti M (2008), 'Multifunctional membranes based on spinning technologies: the synergy of nanofibers and nanoparticles', *Nanotechnology*, 19, 285707.

Schreuder-Gibson HL, Gibson P, Senecal K, Sennett M, Walker J, Yeomans W, and Ziegler D (2002), 'Protective textile materials based on electrospun nanofibers', *Journal of Advanced Materials*, 34 (3), 44–55.

Schreuder-Gibson HL, Truong Q, Walker JE, Owens JR, Wander JD and Jones Jr WE (2003), 'Chemical and biological protection and detection in fabrics for protective clothing', *MRS Bulletin*, 574–578.

Sojka-Ledakowicz J, Lewartowska J, Kudzin M, Leonowicz M, Jesionowski T, Siwinska-Stefanska K, and Krysztafkiewicz A (2009), 'Functionalization of textile

materials by alkoxysilane-grafted titanium dioxide', *J Mater Sci*, 44 (14), 3852–3860.

Sundarrajan S and Ramakrishna S (2007), 'Fabrication of nanocomposite membranes from nanofibers and nanoparticles for protection against chemical warfare stimulants' *J Mater Sci*, 42, 8400–7.

Sundarrajan S and Ramakrishna S (2010a), 'Fabrication of functionalized nanofiber membranes containing nanoparticles', *J Nanosci Nanotech*, 10, 1139–47.

Sundarrajan S, Richard A, and Ramakrishna S (2010b), 'An update on nanomaterials based textiles for protection and decontamination', *J Am Ceram Soc*, 93, 3955–75.

Sundarrajan S, Murugan R, Sreekumaran Nair AN, and Ramakrishna S (2010c), 'Fabrication of P3HT–PCBM solar cloths by electrospinning technique, *Mater Lett*, 64, 2369.

Utamapanya S, Klabunde KJ, and Schlup JR (1991), 'Nanoscale metal oxide particles/clusters as chemical reagents. Synthesis and properties of ultrahigh surface area magnesium hydroxide and magnesium oxide', *Chem Mater*, 3, 175–181.

Wang XD, Summers CJ, and Wang ZL (2004), 'Large-scale hexagonal-patterned growth of aligned ZnO nanorods for nano-optoelectronics and nanosensor arrays', *Nano Lett*, 4, 423–426.

Wu J, Zhou D, Doo CO, Wallace GG (2005), 'Conducting polymer coated lycra', *Synth Met*, 155, 698–701.

Wu Y, Alici G, Spinks GM, Wallace GG (2006), 'Fast trilayer polypyrrole bending actuators for high speed applications', *Synth Met*, 156, 1017–1022.

5
Smart barrier membranes for protective clothing

P. I. DOLEZ, École de Technologie Supérieure, Canada

Abstract: As a way to protect against dermal exposure to chemical and biological hazards, barrier materials have been designed to be used in protective clothing. However, several problems remain; for example, breathability, functionality, performance and durability. Smart membranes based on technologies such as nanomaterials, electrospinning, graft polymerization, N-halamine compounds, etc. offer some promising solutions to these needs; in particular, in providing responsive and self-decontaminating capabilities. Yet numerous challenges still exist before getting to the ultimate goal – an adaptive membrane that rapidly adjusts in a reversible way to environmental conditions and threat intensity.

Key words: chemical and biological protective clothing, responsive barriers, self-decontaminating membranes.

5.1 Introduction

Chemical and biological protection remains a major issue, especially at work. In Europe, almost half of occupational deaths are attributed to exposure to dangerous substances (Brun *et al*., 2009). That number could even be an underestimate, as some suggest that the magnitude of work-related cancers might be two to three times those that are currently reported. A relation between the use of household chemicals and the incidence of cancer has also now clearly been established (Zota *et al*., 2010). One challenge with chemical and biological protection arises from the fact that the number of pure products and mixtures is huge and is always increasing. The list of emerging chemical risks includes ultrafine and nanoparticles, diesel exhaust, man-made mineral fibers, epoxy resins and isocyanates (Brun *et al*., 2009). The variety of exposure situations, entry routes into the human body, adverse effects, individual responses, as well as combinations with other hazards only add to the difficulty. Among the entry routes, which also include inhalation and ingestion, dermal absorption is reported as the most prevalent in the case of occupational exposure to chemicals (Obendorf, 2010).

As a way to provide protection against dermal exposure to these chemical and biological hazards, barrier materials have been designed to be used

in protective clothing. They are intended to limit or block the passage of designated compounds, which can be in solid, liquid or gaseous form (Wales, 2002). In the case of chemical hazards, exposure may involve continuous contact with liquids or intermittent splashes, particles of various sizes in aerosol, powder or liquid suspension, gas, vapors, etc. (Carson and Mumford, 2002). Biological hazards, for their part, include fungi, bacteria and viruses (Wales, 2002).

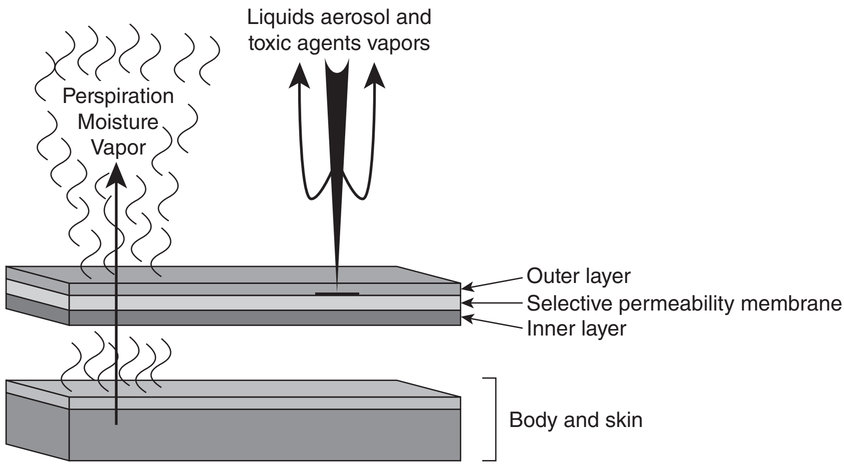
Barrier material resistance to chemical and biological hazards includes three aspects (Stull, 2005): degradation, penetration and permeation. Degradation corresponds to a modification in the material's properties. Penetration involves a flow of matter through closures, seams, pores and defects. Permeation takes place at the molecular level. In addition to the resistance to chemical and/or biological agents, barrier materials must also generally fulfil other requirements; for example, resistance to mechanical, thermal, electric/electrostatic, vibration and radiation hazards (Dolez *et al.*, 2010). Functionality and comfort are a major concern too, as they affect the way the protective clothing interferes with task completion as well as the wearer's well-being. Material properties controlling functionality and comfort of protecting clothing include stiffness, adherence and breathability. The latter is a particular challenge for barrier membranes as air and water vapor need to be allowed to cross in one direction for proper cooling while chemicals and biological agents should be prevented from entering the protective clothing.

The current technology for protection against chemical and biological hazards is based on four approaches (Truong and Wilusz, 2005) using:

- impermeable fabrics,
- semipermeable membranes,
- air permeable membranes,
- selectively permeable materials.

The first approach consists in a complete sealing of the wearer from the environment. This can be accomplished with the use of impermeable film-laminated fabrics, e.g. in fully encapsulated HAZMAT suits (Schreuder-Gibson *et al.*, 2003). However, comfort and heat stress may become an issue for long periods of operation or at high workload.

An alternative strategy involves the use of a semipermeable membrane combined with a repellent surface treatment and an adsorptive liner (Obendorf, 2010). This allows some water vapor and air exchange while limiting chemical and biological compound entry. These semipermeable membranes, which act as a filter, may be either textile-based or made of monolithic or microporous polymers. In general, better protection but lower air permeability is achieved with microporous membranes than with fibrous ones (Obendorf, 2010).



5.1 Schematic representation of the selective permeability principle. (Reproduced with permission from Dolez, 2009. Copyright 2009 CIOP–PIB.)

Air permeable membranes may also be used for better cooling. However, they do not provide any significant protection against liquids, aerosols and vapors, and are generally combined with an adsorptive layer and a liquid/aerosol-proof over-garment (Truong, 2005).

Finally, selectively permeable materials have recently been developed (Zukas, 2004; Schreuder-Gibson, 2003; Truong and Wilusz, 2005). They are based on multilayer composite systems and allow selective permeation of water vapor from the body while preventing the entry of chemical and biological hazards in liquid, vapor and aerosol forms (see Fig. 5.1). The use of selectively permeable membranes generally leads to a reduction in weight and bulkiness of the protective clothing.

In the case of polymer membranes, different types of mechanisms take place depending on the state of the penetrant. Filtration of solid particles involves size exclusion, charge exclusion, depth and chemical interaction (Guillen and Hoek, 2010). Particles larger than the pore size are mostly blocked while smaller ones get through. However, particle capture generally leads to a progressive and irreversible clogging of the membrane, modifying rapidly its breathability performance, as well as its other properties. Penetration of gas through polymer membranes is a diffusion-controlled process governed by Fick's law (Brown, 2001). Selective penetration is achieved as each gas progresses according to its own rate of diffusion. Transport of liquids through polymer membranes proceeds through adsorption, absorption, incorporation into micro-voids, cluster formation, solvation-shell formation and other modes of mixing, diffusion through pores and free volume, and finally desorption on the other side (Comyn, 1985).

Crystalline phases are excluded from the sorption and diffusion process and thus lead to a reduction in the penetration rate. On the other hand, if a liquid plasticizes the polymer, chain mobility is increased, which raises the penetrant diffusion rate through the membrane. Polymer swelling by the solvent further adds to the process complexity.

Materials currently used to produce polymer membranes for chemical and biological protection are mostly based on fluoropolymers, such as polytetrafluoroethylene (PTFE) and Viton®, polyurethane, polyvinylchloride, chlorinated polyethylene, polyethylene, butyl rubber, nitrile rubber and Neoprene (Fatah *et al*., 2007; Stull, 2005). Microporous membranes are usually obtained by dry-cast, wet-cast or dry–wet cast processes (Nguyen *et al*., 2010). The microporous structure is generally produced as a result of a phase inversion phenomenon involving immersion in a non-solvent bath or the evaporation of a solvent from the polymer solution. Nanoporous, butyl rubber-based, breathable membranes have also been obtained by blending and copolymerizing with a cross-linkable liquid crystal monomer (Jin *et al*., 2005).These polymer membranes can be coated, laminated or glued onto a textile structure for mechanical support (Stull, 2005).

Penetration of liquids through textile-based barriers involves capillary action. It is controlled by pore size and structure, fiber chemistry and surface treatments, as well as the surface tension and viscosity of the penetrating liquid (Obendorf, 2010). In the case of aerosols, filtration relies on six mechanisms: diffusion due to particle Brownian motion, direct interception, gravitational deposition, inertial projection, electrostatic interaction and finally Van der Waals molecular force effect (Pich, 1966). The filter characteristics affecting the filtration efficiency are its thickness and porosity, as well as the diameter of the fibers. The properties of the particles (size, shape, density and charge) and of the carrier gas (flow, pressure and temperature) also have a large effect. A major problem with aerosol filtration using fibrous filters is the progressive clogging of the structure with the filtered particles leading to the modification of its performance.

Nonwovens currently represent a major part of the textile materials used in chemical and biological protective clothing, especially for disposable garments (Butler, 2000). One of the most popular nonwoven technologies is based on flashspun polyethylene, according to a process developed by DuPont and manufactured under the brand name Tyvek® (DuPont, 2005). Another one involves the three-layer spunbond/meltblown/spunbond polypropylene structure marketed by Kimberly Clark under the name Kleenguard® (Kimberly-Clark, N.D.). These materials are relatively cheap, offer a reasonable breathability, and have demonstrated some efficiency against particles and water-based liquids (Stull, 2005). Some woven materials are sometimes encountered in chemical and biological protective clothing. With

a very tight weave and a repelling treatment, they can offer a minimal protection against liquids (Stull, 2005).

Sorption liners are often used to provide chemical protection against vapors for clothing based on air-permeable or semipermeable membranes. Activated charcoal or other adsorbents are impregnated into a polymer foam or dispersed in a textile nonwoven, in order to trap the toxic chemicals (Truong and Wilusz, 2005). They can take, for example, the form of activated charcoal beads or encapsulated carbon spheres (Fatah *et al.*, 2007). They can be further impregnated with metal oxides, such as Ag, Cu, Zn and Mo, in the presence of triethylenediamine to give them additional chemical reactivity for high vapor pressure agents (Sundarrajan *et al.*, 2010). Research in that area includes the development of sol–gel derived carbon xerogels, used as a coating on plasma-treated polypropylene fabrics (Cireli *et al.*, 2006). These solid carbon materials, produced by low temperature drying of resorcinol with formaldehyde, display a controlled, high surface area, porous structure and can be used as adsorbents for volatile organic compounds (VOCs). However, the additional liner provides only a limited level of protection and its bulkiness contributes to the heat stress issue.

These different types of materials and structures may also be combined for improved protection against chemical and biological toxic agents. For example, protective garments for emergency first-responders generally comprise a woven or nonwoven membrane, which can be made of polyolefin, polyamide or aramid, coated on the inside and on the outside with layers of fluoropolymers, elastomers or other liquid and vapor-resistant polymers (Fatah *et al.*, 2007). Multilayer systems are also used as the basis of the newly developed permselective membranes, which combine the barrier capabilities of various polymers including cellulose, PTFE, polyallylamine and polyvinyl alcohol (Truong, 2005). For example, the company DuPont™ is working on technologies relying on nonwovens made of spun polymers (DuPont, 2007). For its part, W. L. Gore & Associates counts on expanded-PTFE-based multilayer polymer membranes for their ChemPak® products (W.L. Gore and Associates, 2011).

Ideas in development include the use of hollow fiber composite membranes (Brown, 2001) and of fiberglass as support for PTFE laminates (Stull, 2005). Work is also in progress to produce a selectively permeable membrane that combines protection against hazardous chemical and biological agents and breathability by coating a microporous nylon membrane with a nanofibrous polyacrylonitrile web (Gowayed *et al.*, 2006). Finally, ion beam modification of membranes for increased permselectivity has also been investigated, with nitrogen and fluorine ion implantation of Nafion® (Zukas *et al.*, 2004).

Chemical and biological protective clothing can be classified according to its design, i.e. its configuration and the body part it protects, its

performance and its length of use (disposable, limited use and reusable) (Stull, 2005). A series of standard methods are available to characterize its resistance to degradation, penetration and permeation when exposed to chemical and biological hazards. They include tests performed on the clothing material; for example, the measurement of the resistance to permeation by liquids and gases under continuous contact (ASTM, 1999) or the penetration by blood-borne pathogens (ASTM, 2003). Some test methods also evaluate the performance of clothing parts and full ensembles because seams, closures and interfaces may be the weak link of the clothing system (Stull, 2005). In addition, requirements for chemical and biological protective clothing include specifications relative to physical, mechanical and ergonomic properties. A detailed list of relevant methods can be found, for example, in Stull (2005). Particular requirements and test methods also exist for some types of professional activities; for example, NFPA 1994 for first-responders to CBRN (chemical, biological, radiological and nuclear) terrorism incidents (Truong and Wilusz, 2005).

However, these various test methods may not be representative of all conditions encountered during use that may affect protection (Stull and McManus, 2005). For example, it has been shown that the transport rate of chemicals in liquid and vapor form, including water vapor which controls breathability, may be strongly modified by the humidity level, depending on the type of material (Gibson and Schreuder-Gibson, 2009). These test methods also do not generally include an evaluation of the durability of the material and clothing as a result of service use (Stull and McManus, 2005).

There are still numerous challenges with protective clothing and, in particular, with protection against chemical and biological hazards (Dolez and Vu-Khanh, 2009). Current needs include lighter, thinner and more air-permeable membranes (Duncan, 2006) and improved durability (Scoble, 2011), as well as multifunctionality (Gomes, 2009). One problem with the current technologies is also that, once the barrier membrane is cast, its properties are set, which renders its selectivity static. This situation limits the action on thermal stress as protection levels cannot adapt to danger intensity. In addition, when membranes have been in contact with the chemical and biological toxic agents, they become contaminated, which limits their length of use and induces the risk of secondary contamination.

Since the concept of smart materials was first introduced in 1989 (Kiekens *et al.*, 2004), they have found a wide range of applications in protective clothing, thanks to their capacity to sense, react and adapt to a large number of stimuli: electrical, magnetic, thermal, optical, acoustic, mechanical, chemical, etc. (Van Langenhove *et al.*, 2005). In particular, they can contribute to increased safety by detecting dangerous conditions, sending out a warning signal and reacting by providing instantaneous protection. These three levels of functionality define the three categories of smart materials: passive

with only sensing capability, active with both sensor and actuator functionalities, and ultra-intelligent, the third generation of smart materials able to sense, react and adapt to external stimuli (Begriche and Lachapelle, 2010). Since some materials are sensitive to chemical and biological compounds, smart clothing can be designed to provide protection against chemical and biological hazards. In particular, it is possible to take advantage of their responsive and self-decontaminating capabilities to provide an answer to some of the needs identified with chemical and biological protective clothing.

5.2 Principles and types of responsive barriers

Responsive barriers can be defined as chemical and biological protective systems undergoing changes upon exposure to defined stimuli (Popa *et al.*, 2009). They thus should combine sensing and reacting functionalities. When dealing with chemical and biological hazards, a number of indicators can be used as stimuli: the chemical nature of the compound, its pH, its ionic strength, its heat of reaction, its moisture content, its surface tension, its biological surface functionalities, etc. Various types of smart materials are available with properties activated by these stimuli; for example, electrically conductive polymers, thermally active aerogels, chromic materials, active adsorbents and shape change materials (Janssen, 2008).

Sensors represent a first stage for the development of smart clothing for chemical and biological protection. One type of technology that has raised a lot of interest is based on conducting polymers (Schreuder-Gibson *et al.*, 2003). For example, doped polypyrrole, polythiophene and polyaniline can be used as sensors for the detection of volatile and liquid chemicals. The principle of these sensors relies on the doping/de-doping mechanism that takes place when they are exposed to oxidizing/reducing agents. The presence of contaminants can be detected by monitoring the resistivity of the conductive polymer. A high sensitivity to toluene vapor combined with a good response time and an excellent reversibility has been obtained with octa-aniline doped with dodecylbenzenesulfonic acid and spun cast from a solution in chloroform (Feng and MacDiarmid, 1999). This sensor also displayed a very small sensitivity to water vapor, which often induces interference problems during the detection of VOCs. These types of conductive polymers have also been successfully applied as coatings on optical fibers (El-Sherif *et al.*, 2000). The photochemical sensor produced by locally replacing the cladding layer of an optical fiber by a polyaniline thin film about 2.5 μm thick turned green when exposed to hydrochloric acid (HCl) vapor and blue when exposed to ammonium hydroxide (NH_4OH).

Carbon nanotubes can also be used to produce conductive polymer composite fibers working as chemical sensors (Devaux, 2007). A successful

selective detection of chloroform, methanol, toluene, tetrahydrofuran, and styrene vapor was achieved with a nanocomposite yarn made of 1% of multiwall carbon nanotubes (MWCNT) dispersed in a polycarbonate matrix (Mezzo, 2009; Devaux, 2007). The reaction time was a few minutes and good reversibility was observed over several cycles.

A further improvement for these conductive polymers lies in the production of conducting nanofibers, for example those obtained by electrospinning (Schreuder-Gibson *et al.*, 2003), as well as in the development of nanocomposites such as polyaniline nanofibers in a matrix of chitosan (Li *et al.*, 2011) and hybrid materials (Itoh *et al.*, 2008). In particular, layered organic–inorganic nanohybrids based on molybdenum trioxide thin films, intercalated with polyaniline, were able to detect concentrations of formaldehyde and acetaldehyde as low as 25 ppm.

Titanium dioxide nanostructured thick films produced by screen-printing of nanotubes also display interesting gas detecting capabilities (Seo *et al.*, 2009). Discrimination between carbon monoxide, hydrogen, ethanol and toluene was successfully achieved, with a good response time. An alternative technique makes use of the surface plasmon resonance (SPR) band, which is observed in the absorption spectrum of several metallic nanoparticles (Duncan, 2006). A shift in the SPR peak was obtained when a gold nanoparticle film was exposed to organic vapor. These various types of sensors can be further incorporated into textile structures, for example by weaving, knitting or as a coating or laminate (Begriche and Lachapelle, 2010). Finally, enzymes can be used to detect organophosphates, commonly referred as nerve agents (Russel *et al.*, 2003). A sensor developed by the company Agentase, combines acetylcholine, acetylcholinesterase, urea, urease, and a pH-sensitive dye. It offers a fast and strong response, as well as a high resistance to interference by temperature.

As a complement to sensors for producing responsive barriers, actuators can be designed using several promising technologies. One of the best known employs shape memory materials (SMMs). These are able to change their shape in a reversible way under various types of stimuli; for example, heat, stress or pressure, electrical current or voltage, light, magnetic field, the presence of a solvent or a change in pH or moisture content (Sun *et al.*, 2011). SMMs can be made of alloys, in which the shape memory effect is produced by a reversible martensitic transformation, or of polymers with a dual segment/domain structure. One segment/domain is fixed and elastic while the other one undergoes a reversible transition from stiff to soft, under the application of the stimulus.

The major advantages of shape memory polymers over alloys for protective clothing include their low density, their lower cost for raw material and manufacture, their very high recoverable strain, their high flexibility in terms of shape and properties, their excellent chemical stability and the

possibility that they can be activated by more than one stimulus. However, their actuation stress is only a few MPa.

Among the polymers that have shown shape memory properties (for example trans-polyisoprene, poly(styrene-co-butadiene) and polynorbornene), segmented polyurethane, which can be easily processed, has raised most of the attention (Hu, 2007). Shape memory polyurethane actuators were successfully produced as thin film (Fenglong *et al.*, 2006), foam (Sung Ho *et al.*, 2007) and fiber (Fenglong *et al.*, 2006; Hu, 2007). In particular, it was shown that fibers produced by wet spinning display a preferential orientation of the molecules in the fiber axis direction, which induces an aggregation of the fixed segments into fixed domains and an improvement of the shape recovery compared with films (Fenglong *et al.*, 2006).

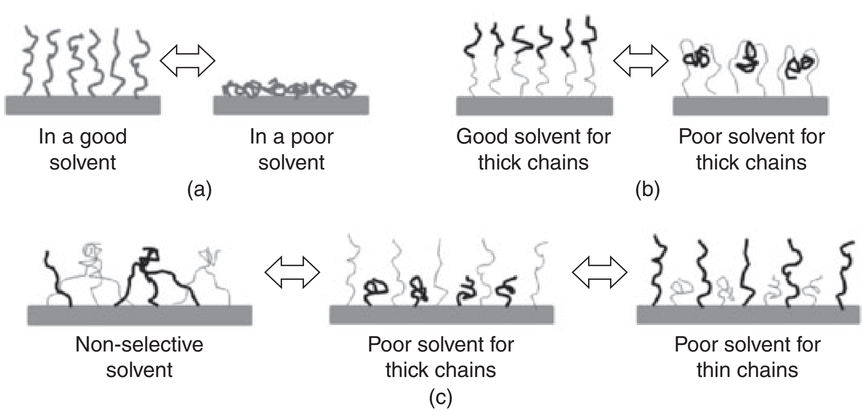
In addition to the well known thermally activated shape memory effect observed in segmented polyurethane (which can be attributed to the switch between hard and soft for the transition segments/domains at their glass or melting temperature and can be used to produce temperature-adjustable breathable membranes (Hu, 2007)), SMM polyurethane has been observed to be sensitive to moisture (Sun *et al.*, 2011). Bonded water was identified as the driving force for this effect. Moisture content was found to affect the glass transition temperature and stress/strain behavior of SMM polyurethane foams (Yu *et al.*, 2011). A strong water-induced shape memory effect was also observed in poly(vinyl alcohol) (PVA) chemically cross-linked with glutaraldehyde (Du and Zhang, 2010). This polymer is also sensitive to organic solvents as a result of the swelling generated in PVA by some solvents.

The development of composite SMMs has allowed improving actuator performance and multifunctionality (Leng *et al.*, 2011). For example, the introduction of MWCNTs into SMM polyurethane, and the production of fibers after *in-situ* polymerization and melt-spinning, further increased the shape recovery ratio and time of the material (Meng and Hu, 2008). This effect was attributed to the internal elastic energy storage and release capability of the preferentially fiber-axis-aligned MWCNTs. Composite materials have also created a new class of SMMs, shape memory hybrids (Sun *et al.*, 2011). In that case, the elastic-transition segment/domain system is provided by the two composite material components; for example, an elastic matrix and transition inclusions. The properties of such shape memory hybrid materials are much easier to predict and control, especially if no chemical interaction exists between the matrix and the inclusions.

Polymer gels and elastomers also offer an interesting potential as actuators for chemical and biological protection because of their adjustable degree of swelling in solvents (Hirai *et al.*, 2001). They may be triggered by physical stimuli as well as by chemical ones, in particular pH, oxidation/reduction, solvent exchange and ionic strength. For instance, pH-sensitive

hydrogel fibers based on polyacrylonitrile exhibited contractions and dilatations when exposed alternatively to hydrochloric acid and sodium hydroxide, with a reaction time of 45 s (Brock *et al*., 1994). Other types of hydrogels have since demonstrated some pH-responsive properties; for example, poly(acrylic acid-co-acrylamide) grafted chitosan and poly-(dimethylaminoethyl methacrylate-co-unsaturated carboxylic acid) (Tondu *et al*., 2009). Improvement over the years has led to shorter reaction times, to a few tenths of a second (Van Langenhove *et al*., 2005). Finally, modified textiles containing crosslinked polyols display a dimensional memory effect associated with wet shrinkage occurring in various solvents such as hexane, acetone, ethanol, and water (Vigo and Thibodeaux, 2001). These can be used to design actuators sensitive to chemical and biological hazards.

A first avenue for producing responsive chemical and biological barriers is to control the surface properties of the material; in particular, to provide it with active repellent capabilities. Among the various types of surface modification methods available, the grafting technique offers the advantages of an easy and controllable attachment of a wide range of polymer chains with a high surface density, the precise location of these chains on the material surface, and a high stability of these grafted chains thanks to covalent bonding (Luzinov, 2007; Minko and Motornov, 2007). In particular, polymer brushes, which are attached to the surface by one chain end, adapt to their environment by modifying their conformation as a result of a phase segregation mechanism. For example, they may switch from a folded coil configuration to an extended coil one as a result of a change in solvent nature, pH, ionic strength, polarity, etc. (see Fig. 5.2.a). However, these homopolymer brushes affect only the quantitative composition of the surface. In order to modify the nature of the surface, two alternative

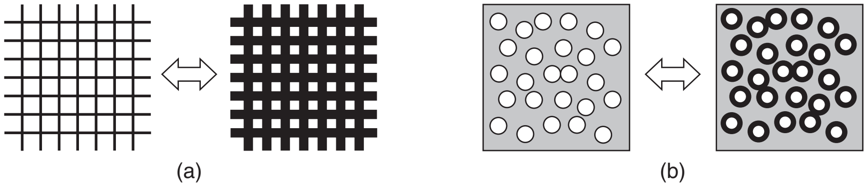


5.2 Different categories of polymer brushes. (a) Homopolymer, (b) copolymer, (c) mixed polymers. (Adapted from Minko, 2007.)

approaches can be used. First, brushes can be produced using block-copolymers. The change in surface properties occurs as the end block coils inside the attaching block (see Fig. 5.2.b). In addition, different types of polymers can be grafted onto the surface to give mixed brushes. In that case, the number of configurations increases, with different surface conditions being exhibited depending on the folded or extended conformation of each polymer (see Fig. 5.2.c). Response times of a few seconds make these polymer brushes choice candidates for the development of responsive barriers. They have been successfully applied as coatings on various types of surfaces, including fibers and textiles of cotton (Zheng *et al.*, 2011), polyethylene terephthalate and nylon (Burtovyy, 2008). In some instances, a more pronounced switching effect is observed as a result of the amplification produced by the textile surface texture (Minko and Motornov, 2007).

Polymer brushes can also be grafted onto the surface of colloidal particles, which are then covalently attached to the fiber surface using well-mastered technologies for pigment deposition on textiles (Motornov *et al.*, 2007). In addition, polymeric ionic liquids can also be used to produce responsive polymer brushes (David, 2011). For example, an adjustable surface wettability was obtained by exposing the polycationic brush-grafted samples to different anions. Such behavior is especially valuable for protection against biological hazards since there is a direct correlation between surface wetting by water and microorganism penetration (Obendorf, 2010).

A second avenue for designing responsive barriers takes advantage of the capacity of some polymers to selectively swell in solvents and of the impact this has on transport through porous membranes. In fact, one of the first models of water-resistant, breathable fabrics, known as Ventile®, consisted of a tightly woven cotton structure in which the fibers swelled when exposed to water and limited its penetration through the membrane (Keighley, 1985). More recently, developments have involved the use of superabsorbent polymers to design chemical and biological fibrous barriers with active swelling behavior (see Fig. 5.3.a). For example, polyacrylates, and polyacrylamide in particular, display a very large absorption capability with fast kinetics (Liu and Zhou, 2002). Interesting swelling properties were



5.3 Swelling-induced responsive behavior with (a) fibrous membranes, and (b) polymer porous membranes.

also observed with a thermoplastic surface-interpenetrating network of poly(ethylene terephthalate) (PET) and polyacrylamide (PAM) after swelling in a mutual solvent and *in-situ* polymerization of the PAM monomer (Liu, 2010; Liu *et al.*, 2010). A large reduction in the interfiber pore size of the treated PET fabric was obtained in the swollen state in water. The amide-immobilized chains can further be converted to a biocidal agent for a complementary protection action. This technique thus displays a strong potential for biological protection.

Variable pore size membranes can also be designed by grafting responsive polymers onto porous substrates (see Fig. 5.3.b). For example, the surface of a microporous polyurethane (PU) membrane was grafted in a two-step functionalization/polymerization process with poly(ethylene glycol) (PEG) (Tan and Obendorf, 2006). The change in water vapor permeability with moisture content was attributed to the swelling of the hydrophilic PEG chains grafted within the PU membrane pores. However, response times need to be shortened for practical applications as chemical and biological protective barriers.

Nanocomposite membranes consisting of a nanoporous hydrophobic matrix grafted with a hydrophilic polyelectrolyte have also been produced for stimuli-responsive, breathable properties thanks to the chemical-selective swelling of the polyelectrolyte (Chen, 2005). An increase in selective transport of water vapor over dimethyl methylphosphonate vapor by twelve times and a water vapor transmission rate two to four times higher than the acceptable breathable level were obtained with track-etched polyester and two polyelectrolytes, poly(methacrylic acid) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid). Membranes with pore size responsive to a change in pH were obtained by plasma and radiation grafting of acrylic acid and N-isopropylacrylamide on porous polyamide and polysulfone samples (Lee and Shim, 2001).

Another more drastic metamorphosis with exposure to liquids has been reported with polymeric ionic liquids (David, 2011). Solvent-reversible poration is obtained when the system goes from porous to hydrogel, and *vice versa*, upon exposure to organic solvents and water, respectively. The principle behind this phenomenon lies in the phase separation of the copolymer containing a polar imidazole group and a hydrophilic tail, as well as the anion exchange mechanism present in polymeric ionic liquids. Pore closure in that system occurs as a result of swelling of the shrunken copolymer at the interface with water and displays a strong selective character; it was achieved only with water-miscible solvents.

Several other technologies have also been envisioned for active selective permeability. For example, the physicochemical properties of polymeric ionic liquids are strongly affected by the anion exchange reaction (David, 2011). Their permeability to gases, whose selectivity has been improved by

the formation of composites with cross-linkable ionic liquids, may thus be controlled by exposure to different ion solutions. Interpenetrating polymer network hydrogels (IPNH) also display an adjustable permeability, which depends on the swelling level of the material (Lee and Kim, 2001). A high permeability is obtained when the hydrogel is swollen. This swelling may be activated by pH, ionic strength and contact with chemicals among others. For example, IPNHs based on PVA and poly(acrylic acid) displayed a good sensitivity to pH of their swelling ratio and penetrant transport.

An alternative concept is based on the use of electrically conductive porous polymer membranes (Guillen and Hoek, 2010). The application of an electrical potential across the membrane induces an in-pore electrical field that may affect the transport of a solute, depending on its charge. In some preliminary experiments, polyaniline–polysulfone porous membranes were produced with various ratios of the two components, and were tested for silica nanoparticle rejection from feed water using constant and pulsed electrical potentials. Some variations in nanoparticle rejection with potential amplitude and mode were observed.

Electrical actuation may also be used with nanoporous polymer membrane composites grafted with ionic gels (Elabd and Palmese, 2007). The ionic gel located within the nanopores contracts and expands in response to the application of the electrical field, thus providing a way to adjust the pore size as required. In addition, the use of water permeable, ionic gels allows a high level of breathability. Results are reported for a nanoporous, track-etched polyester grafted with poly(2-acrylamido-2-methyl propane sulfonic acid). They show a reversible shift in the membrane permeability to dimethyl methylphosphonate (DMMP), (which is used as a surrogate for the nerve agent sarin) with the application of the electrical actuation. A ten-fold increase in DMMP versus water vapor selectivity compared with the Joint Service Lightweight Integrated Suit Technology (JSLIST) system currently used by the US military for protection against chemical and biological agents, radioactive fallout particles and battlefield contaminants, was also observed, while the water vapor transmission rate was similar.

Finally, a proposed concept making use of electrical actuation to vary permeability to gases, liquids and particles is based on a system composed of two membranes (Trentacosta and Kapur, 2009). Upon electrical actuation, the holes of the second membrane come out of registration with the holes of the first membrane, thus decreasing the permeability. An alternative solution relies on protrusions in the second membrane to block, on command, the holes in the first membrane.

One aspect where significant progress towards the development of commercial products has been achieved, deals with chemical and biological barriers offering responsive breathability. Water vapor transport through

tightly woven fabrics and microporous polymer membranes is principally controlled by diffusion (Lomax, 1985). On the other hand, it involves a combination of molecular diffusion through transient inter-chain pores and bonding–debonding with hydrophilic side groups in the case of monolithic polymer films. It has been estimated that, at high work rates, about 500 watts must be dissipated by water evaporation, which corresponds to an evaporation rate of 19 000g of water per 24 h (Keighley, 1985). However, measurements carried out with 25 models of breathable fabrics based on polyurethane coating, PTFE laminate, and water-swelling proofed cotton, showed levels of water vapor permeability that were clearly insufficient to achieve proper cooling at these high workloads. An interesting solution to adapt water vapor permeability to temperature changes takes advantage of the temperature activated shape memory effect in polyurethane membranes (Hu, 2007). Below its transition temperature, the membrane displays very low water vapor permeability. However, when the temperature increases, the shape memory effect leads to a rise in free volume, which augments the water vapor permeability. Promising results have been reported with a polyurethane based on 4,4-diphenylmethane diisocyanate, poly(ethylene glycol) (PEG), polybutylene adipate and 1,4-butanediol (Lin *et al*., 2007). A sharp increase in water vapor permeability was observed above 18 °C. A commercial thermo-responsive breathable membrane based on shape memory polyurethane has been developed by Mitsubishi Heavy Industries (SMP Technologies Inc, 2010). Thermally-activated micro-brownian motion leads to the formation of free volume with increased temperature, which allows water vapor molecule transport. The membrane can be laminated onto various types of textiles to be used as waterproof, windproof yet breathable clothing. Another system has been developed by Ahlstrom Corp. and includes a temperature-responsive, breathable, monolithic film, sandwiched between two layers of spunbond microfibrous polypropylene (Rodie, 2005).

In terms of production methods, electrospinning offers a very large potential for the production of smart polymer fibers. Indeed, it is an easy up-scalable process and the produced fibers display an extremely high surface area, which enhances responsiveness (Popa *et al*., 2009). Electrostatic spinning consists of drawing a polymer melt or solution from a nozzle to a collector by application of an electrical field. Fibers with diameters between 40 nm and 2 μm can be produced by selecting the right combination of polymer, solvent and spinning conditions (Grafe and Graham, 2002). They can be further functionalized to provide them with the desired specific properties. Nanofibers produced by electrospinning have been successfully functionalized by various techniques (Wang *et al*., 2009). In particular, plasma-based treatments have raised a large interest. Indeed, as dry processes, they offer significant financial and environmental

advantages compared with traditional wet textile finishing (Marcandalli and Riccardi, 2006). They make use of gases ionized by application of high voltages between electrodes. Atmospheric cold plasma treatments can easily be incorporated into textile production lines. In addition to changing the surface properties, the plasma technique can also be used to prepare a surface before applying another surface modification treatment (John and Anandjiwala, 2009). For example, plasma activation can be followed by graft polymerization. For that purpose, graft polymerization constitutes a choice method for tailoring chemical and physical properties, and functionalizing surfaces in a reliable way (Olivier *et al*., 2012). It is a very versatile technique since it applies to a wide range of polymers. The homopolymer and block copolymer brushes that are obtained can also be used to provide responsive functionalities to surfaces (see Fig. 5.2). They may also be located inside the pores of microporous membranes and impart them with active selective permeability. Other novel technologies have been identified for the production of smart materials (Gomes, 2009): inkjet printing for the integration of electroactive materials directly onto polymer and textile surfaces; bi- and tri-component fibers for integrated sensor and actuator applications; multifunctional coating combining, for example, ultrasonic deposition, electron-beam polymer layer deposition, metal evaporation; DC sputtering and chemical vapor deposition; and hot-melt coating with functional nanomaterials.

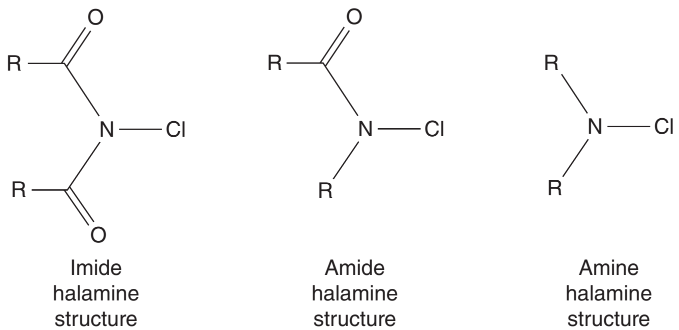
5.3 Principles and types of self-decontaminating barriers

One step further for adaptation to stimuli is neutralizing the effect of the threat (Van Langenhove *et al*., 2005). An example is heat, with cooling or warming functions providing thermoregulation when necessary. It may also involve the degradation of the toxic chemical or biological compound. To that extent, self-decontaminating barriers are currently being developed to automatically destroy chemical and biological toxic agents that come into contact with the protective clothing. The objective is two-fold. First, it avoids putting nearby unprotected people in danger (Schreuder-Gibson *et al*., 2003). In particular, biological warfare agents can attach to clothing and gloves in large quantities and generate extensive secondary contamination when they are further released as aerosols. A second goal is to prevent the progressive clogging of filter-based barriers resulting from being gradually loaded with the contaminants they are screening (Butler, 2000). Indeed this clogging induces a modification of the filter physicochemical properties and affects their efficiency and pressure drop (Pich, 1966). This, in turn, reduces its breathability.

Several self-decontaminating technologies have been identified for clothing that protects against chemical and biological hazards (Cole, 2011; Obendorf, 2010; Sun *et al*., 2008). They include metal and metal oxide particles/nanoparticles, quaternary ammonium salts, polyoxometallates, antibiotics, silver ions, N-halamines, bioengineered enzymes and light activated compounds. Their action proceeds generally either through oxidation, reduction, hydrolysis or disruption of biological functions. However, the applicability of these different solutions for protective clothing is limited by several factors (Schreuder-Gibson *et al*., 2003; Sun *et al*., 2008). First, the self-decontamination compound and degradation products need to be safe for the clothing wearer, which is not the case for free halogens, peroxides at high concentrations and some heavy metals, for example. Second, since toxic threats are generally of multiple nature and sensitive to specific degradation mechanisms, the detoxifying agent needs to be compatible with the complementary compounds used to provide protection against all the potential hazards. Third, biological toxic agents may develop or acquire resistance to the mechanism used to degrade them. This is observed, for example, with families of bacteria becoming antibiotic resistant. Fourth, protection may be progressively lost as the self-decontaminating compound is consumed as a result of its action against the toxic agent. Processes for maintaining the self-decontamination capabilities over the whole clothing service life must therefore be included. Finally, wear and cleaning treatments may induce a premature loss of the active compounds if they are not strongly bonded to the clothing material. All these factors need to be taken into account for the proper design of self-decontaminating barriers to be used in protection clothing against chemical and biological hazards.

A first technology used for self-decontamination relies on N-halamines. Indeed, compounds containing nitrogen–halogen bonds act as oxidizing agents and are thus very effective biocides (Obendorf, 2010). Their mechanism of action is thought to involve a direct transfer of positive halogens to receptors near or at the cell outer membrane. The observed absence of development of resistance to this degradation mechanism may be due to the non-specific oxidation of the functional groups (Schreuder-Gibson *et al*., 2003). Another advantage of this technique is that, after the active compounds have been consumed by the decontamination process, the protective efficiency can be restored by treatment with halogen-releasing chemicals such as sodium hypochlorite, commonly known as chlorox or bleach (Obendorf, 2010).

N-halamines thus offer a large potential for self-decontaminating barriers in protective clothing against chemical and biological hazards, in particular those with imide bonds, which have been shown to display a stronger antimicrobial strength than amides and amines (see Fig. 5.4). However, their apparent sensitivity to light may limit their incorporation in undergarments



5.4 N-halamine imide, amide and amine structures.

and inner surfaces (Schreuder-Gibson *et al.*, 2003). Acrylamide and methacrylamide have been successfully grafted onto cotton cellulose by free-radical polymerization (Liu and Sun, 2006). Their self-decontamination function was further activated by chlorination. A good and rechargeable efficiency against *Escherichia coli* bacteria was observed but the compounds displayed some significant sensitivity to hydrolysis.

The use of cyclic halamines may overcome that issue. Three cyclic N-halamines, chlorinated 5,5-dimethylhydantoin (CDMH), chlorinated 2,2,5,5-tetramethyl-imidozalidin-4-one (TMIO) and chlorinated 3-dodecyl-5,5-dimethylhydantoin, were used as additives during the production of nanofibrous nylon 6 membranes by electrospinning (Tan and Obendorf, 2007a). The best efficiency in terms of contact time for total reduction in *E. coli* and *Staphylococcus aureus* bacteria was obtained with CDMH, which possesses both imide and amide halamine groups. Satisfactory immobilization of the N-halamine additives in the nylon fibers was achieved as no significant leaching was observed. TMIO hydantoin was also grafted onto a functionalized microporous polyurethane membrane (Tan and Obendarf, 2007). Upon chlorination, the antimicrobial efficiency of the N-halamine groups was tested with *E. coli* and *S. aureus*: total reduction was achieved after a 2 h contact period. No significant modification of the water vapor transmission rate as a result of the grafting treatment was recorded.

Finally, an alternative immobilization technique for N-halamines is based on the formation of interpenetrating networks (IPN) (Liu *et al.*, 2010). Thermoplastic surface-IPNs were produced by swelling a poly(ethylene terephthalate) (PET) fabric with methanol containing the vinyl amide monomer and a crosslinking agent, followed by UV polymerization and chlorination. Tests were conducted with acrylamide (AM) and methacrylamide (MAM). Total reduction in *S. aureus* bacteria was obtained after 10 minutes for chlorinated polyAM-PET and after 30 minutes for chlorinated polyMAM-PET. The polyamide molecules were observed to be uniformly distributed along the PET yarns.

A second type of compound used for self-decontamination is based on quaternary ammonium groups. Indeed, bacteria cell walls are generally negatively charged and these polycationic compounds are largely used as biocides (Muñoz-Bonilla and Fernandez-Garcia, 2012). Their mechanism of action usually involves binding to the bacterium, diffusion through its cell wall, degradation of the cytoplasmic membrane, and ultimately cell death. In particular, they display a good efficiency against vegetative bacteria (Schreuder-Gibson, 2009).

Quaternary ammonium groups have been incorporated into polyurethane coatings by crosslinking quaternary ammonium salt diols with polyisocyanate (Wynne *et al.*, 2011). Stronger biocidal activity against Gram-negative bacteria (*E. coli*) was obtained for C8 alkyl films compared to longer chain-length ones. This was attributed to the effect of electrostatic attractive force shielding of the quaternary ammonium groups by the longer alkyl chains, which limited the binding of the bacteria on the film surface. In the case of Gram-positive bacteria (*S. aureus*), longer alkyl chains led to a better decontamination. This method leads to a uniform distribution of the quaternary ammonium salts over the film surface.

Another technique relies on the grafting of tertiary amine polymer brushes onto a microporous membrane, followed by quaternization (Fang *et al.*, 2008). Polypropylene hollow fiber membranes were surface-grafted with block copolymer brushes of poly(ethylene glycol) monomethacrylate (PEGMA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA). The amine groups of the polyDMAEMA were then quaternized with 1-bromodecane. Good biocide activity was observed with *E. coli* and *S. aureus* bacteria. Longer polyDMAEMA chains corresponded to a stronger anti-bacterial efficiency. This was attributed to the higher density of the quaternized ammonium groups on the membrane surface. Repeated bacteria exposure assays displayed similar results, which demonstrated the stability of the anti-bacterial membrane. In addition, since surface functionalization with polyPEGMA leads to a reduction in protein adhesion, the accumulation of dead cells on the membrane surface was minimal.

Quaternary ammonium salts have also been successfully applied to various types of textiles. Nylon fabrics were functionalized with quaternary ammonium salts using acid dyes as bridging elements (Kim and Sun, 2001). Since salt bonds formed by ammonium groups are ionic and potentially soluble in water, the washing durability of the treated fabric was tested. A preservation of 90% of the *E. coli* bacteria reduction after the equivalent of 50 machine washings was obtained with concentrations of quaternary ammonium salts in the finishing solution of 4 to 8%. In addition, 100% of the antibacterial efficiency was maintained after five cycles of bacteria exposure and a Launder-Ometer wash. Quaternary ammonium salts were also used for the production of antimicrobial cotton (Son *et al.*, 2006). The

lack of anionic attractive sites on cotton cellulose for the cationic ammonium compounds was compensated for by the use of a reactive anionic agent. Good antibacterial activity was recorded using *S. aureus*.

Other types of organic compounds have also shown some interesting self-decontamination activity. For example, α-nucleophilic oximes have been shown to hydrolytically decompose organophosphate nerve agents and pesticides (Chen, 2009). Cross-linked polyamidoximate salts were produced by oximation of polyacrylonitrile and polyacrylamide with hydroxylamine hydrochloride, leading to polyacrylamidoxime (known as PANOx) and poly(N-hydroxyacrylamide) respectively, followed by dissociation in water (Bromberg *et al.*, 2009). The efficiency of the polyamidoximate salts was tested with S-2-(diisopropylamino) ethyl O-ethyl methylphosphonothioate (VX), O-pinacolylmethylphosphonofluoridate (soman), and isopropyl methylphosphonofluoridate (sarin). A large increase in the polymer reactivity was observed when exposed to ambient air and 100% humidity. A half-life of less than 3 min for sarin was obtained with PANOx dialyzed in deionized water at pH 12.

Oxime-functionalized fiber mats were produced by electrospinning of polyacrylamidoxime and polyacrylonitrile (Chen, 2009). Hydrolysis of p-nitrophenyl acetate, a surrogate for organophosphate nerve agents and pesticides, by the reactive fiber mat was measured. However, low intra-fiber diffusion limited the accessibility of the oxime groups inside the fibers. In an alternative strategy, polyacrylonitrile submicronic fiber mats were oximated with hydroxylamine, leading to a conversion of the fiber surface into reactive amidoxime sites. The hydrolytic degradation of diisopropylphosphofluoridate (DFP), a surrogate for sarin and soman nerve agents, was measured in the presence of water.

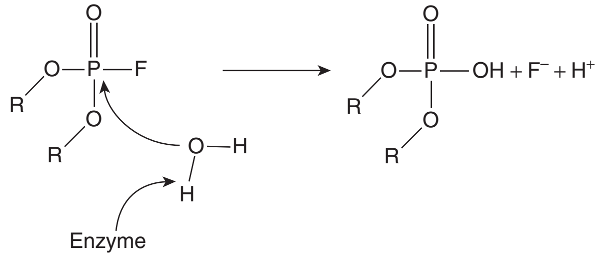
Polyvinylamine (PVAm), a weak cationic polyelectrolyte, has also shown some variable antimicrobial properties, depending on the nature of the hydrophobic alkyl side groups (Muñoz-Bonilla and Fernandez-Garcia, 2012). PVAm with hexyl chains displayed more efficiency against *E. coli* while PVAm with octyl chains was more potent for *Bacillus subtilis*. PVAm-based films with self-decontamination capability for organophosphate nerve agents were produced by blending poly(vinylamine-co-vinyl alcohol) with branched polyethyleneimine and further crosslinking (Schreuder-Gibson, 2009). An increase in the hydrolytic degradation rate of DFP at low relative humidity levels was obtained with the addition of polyaspartate as a result of a two-fold augmentation in water absorption.

Self-decontaminating coatings have also been developed with anti-microbial peptides (Fulmer *et al.*, 2010). These short polypeptides are generally cationic and contain both hydrophobic and hydrophilic domains. They have been shown to display some efficiency against a broad range of bacteria, viruses and fungi, and are thought to be less prone to resistance

development compared to conventional antibiotics. However, they are also toxic to human cells. The study involved the incorporation of two anti-microbial peptides, chrysophsin-1 and chrysophsin-3, as well as their truncated less toxic versions into an acrylic resin, followed by curing. The resulting film displayed 1 to 4 logs reduction in Gram-positive and Gram-negative bacteria counts for the original peptides. In the case of the truncated peptides, the anti-microbial efficiency was reduced by a factor of two for Chrysophsin-1 and totally suppressed for Chrysophsin-3. Alternative strategies need to be identified to lower the toxicity of anti-microbial peptides to human cells without compromising their anti-microbial efficiency.

A final example of organic bactericidal compound investigated for self-decontaminating barrier fabrication is chlorhexidine (Chen, 2009). It was incorporated into cellulose acetate either in the blend before electrospinning or as a post-spin treatment of the fibers through covalent binding with titanium triethanolamine as linking agent. In both cases, an efficiency of 95% or more within 1 hour was measured with *E. coli* and *Staphylococcus epidermis*.

Another technology explored for self-decontaminating barriers is based on the use of bioengineered enzymes. Enzymes offer the advantages of being environmentally benign, functioning efficiently under ambient conditions, and acting as highly effective hydrolysis catalysts (Russel *et al.*, 2003). They are currently one of the best decontaminating solutions for organophosphates or nerve agents, with 10 mg of enzymes degrading as much nerve agent as 1 kg of concentrated bleach. The mechanism of enzyme-catalyzed hydrolysis of organophosphates is illustrated in Fig. 5.5. In addition, since they act as catalysts, they are not depleted overtime. However, enzymes are highly specific and may not be compatible with other biocides (Sun *et al.*, 2008). Furthermore, they generally display a limited stability and must therefore be immobilized for activity preservation during storage and use (Russel *et al.*, 2003). To that extent, polymers represent ideal substrates



5.5 Mechanism of organophosphate hydrolysis catalyzed by enzymes. (Adapted from Ong, 2006.)

for enzymes due to their structural flexibility and good resistance to solvents.

For example, organophosphorus hydrolase (OPH) and organophosphoric acid anhydrolase (OPAA) enzymes have been successfully incorporated into a polyelectrolyte film that can be used as a coating on cotton fabrics as well as on man-made materials (Bealer Rodie, 2006). Coating methods include dip coating, spin coating and spray. A layer of organosilane polymer attracts toxic chemicals to the fabric surface and protects the enzyme-containing film from external stresses. The efficiency of this treatment has been tested with methylparathion, a pesticide (Singh and Dressick, 2006). Degradation activity of the enzymes incorporated into multilayer films made of alternating polyethyleneimine and polyacrylic acid polyelectrolytes was observed to be preserved, even under high humidity environments (up to 85% RH) and after twelve cycles of reuse. The absence of effect of temperature, pH and presence of a solvent was also reported. Genetically-modified OPH was also successfully immobilized on cotton fabrics (Rory, 2007). Hydrolysis of paraoxon, an organophosphate pesticide, and demeton-S, used as a surrogate for VX and RVX nerve agents, was observed at a rate of 21 $\mu g/cm^2/min$ and 5.2 $\mu g/cm^2/min$, respectively.

Encapsulation of enzymes into silica and organically-modified silica has also been investigated (Ong, 2006). Successful OPAA encapsulation was achieved using acid-catalyzed hydrolysis and co-condensation of tetramethylorthosilicate and organosiloxanes. Thanks to the protective mesoporous structure of the enzyme substrate, degradation activity against DFP was observed both in aqueous and mixed aqueous–organic solvents.

Metals have long been used as anti-microbial and antifouling agents. They have also been considered for use in self-decontaminating barriers. For example, iron particles can be used for the containment of chemicals as they reduce oxidized contaminants such as chlorinated solvents, nitroaromatic compounds and heavy metal ions (Shimotori *et al.*, 2004). A membrane was prepared by introduction of 0.1 to 0.2 μm diameter non-oxidized iron particles (Fe^0) in PVA dissolved in water, followed by solvent evaporation and light heat cure. Iron particles were observed to be evenly scattered as 1–2 μm diameter clusters over the membrane surface. A more than 100-fold increase in breakthrough time was measured for carbon tetrachloride and copper ions, which indicates an efficient reaction between iron and these contaminants. This concept could be extended to high-density polyethylene and poly(vinyl chloride) membranes with high potential for self-decontaminating barriers.

Silver also raises a very strong interest since it generates highly reactive ions upon reaction with moisture (Muñoz-Bonilla and Fernandez-Garcia, 2012). Silver ions induce structural changes into protein cell walls and nuclear membranes, leading to cell death. They also form complexes

with DNA and RNA bases and inhibit microorganism replication. Various silver polymer complexes have been produced with excellent anti-microbial efficiency in the solid state against Gram-positive and Gram-negative bacteria. Silver ions have also been complexed with polyoxometalates and used to modify the surface of cotton fabrics (Singh, 2007). The resulting breathable barrier displayed high reactivity against chemical warfare agent simulants, industrial chemicals and pesticides, as well as anti-microbial efficiency against Gram-positive and Gram-negative bacteria.

Dendrimers have also been used to produce silver-ion releasing compounds (Muñoz-Bonilla and Fernandez-Garcia, 2012). For example, silver was solubilized in poly(amidoamine) (PAMAM) and polyester urethanes, leading to anti-microbial efficiency. PAMAM was also employed to encapsulate silver salts; however, it showed a slow release of silver ions. Copper, zinc, manganese, nickel and cobalt are also known as anti-microbial agents. They can be complexed with resins to give, for example, metal polychelates with wide-range antibacterial activity. It is observed that copper complexes are the most active, which is attributed to the higher stability constant of copper ion. Finally, organotin-based polymers have also shown some promising biocide potential; for example, as copolymers with styrene.

In addition to the chemical nature of the self-decontaminating compound, size has also been shown to matter. In particular, nanomaterials (for example nanoparticles and nanofibers) display a much higher reactivity than in bulk, due to their very large surface area (Sundarrajan *et al.*, 2010). In fact, active nanocompounds have been found to adsorb and degrade a large number of toxic chemicals, as well as exhibit an increased bactericidal efficiency. First of all, metal and metal oxide nanoparticles have demonstrated very high performance as degradation catalysts (Sundarrajan *et al.*, 2010). This efficiency is not only a result of their large surface area but can also be attributed to the small size of their crystallites, their unique crystalline morphology, and the presence of large porosities as well as surface defects.

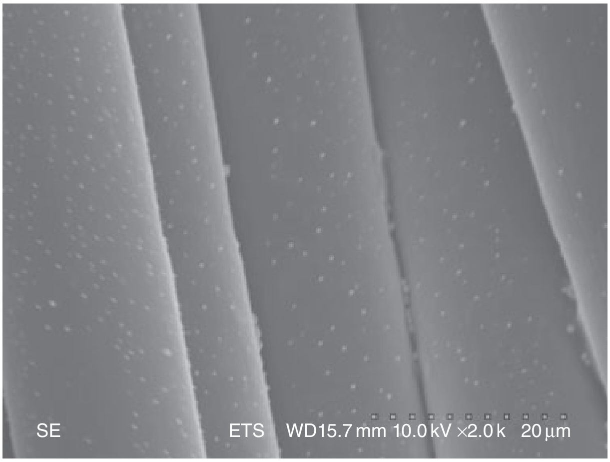
Destructive adsorption of air pollutants, warfare agents, acidic gases, pesticides and other toxic chemicals has been demonstrated for nanoparticles made of magnesium oxide (MgO), calcium oxide (CaO), titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3) and others. Upon adsorption, the compound molecule is chemically modified and made non-toxic. Biocidal activity has also been reported for MgO, TiO_2, silver nitrate ($AgNO_3$) and silver. For example, nanocrystalline MgO particles exhibit a polyhedral structure with a high number of corner and edge sites, which gives them a high reactivity (Obendorf, 2010). They have been shown to degrade dimethyl methylphosphonate, a surrogate for organophosphate toxic agents, and paraoxon. When incorporated into nanofibers, MgO nanoparticles still displayed a catalytic efficiency against paraoxon twice

that of activated carbon (Sundarrajan *et al.*, 2010). This can be attributed to the high surface ratio of the nanofiber host, which allows a low diffusion time before neutralization.

The decontamination of sarin by nanocrystalline zinc oxide (ZnO) has also been studied (Mahato *et al.*, 2009a). It was shown to involve a first adsorption stage, followed by hydrolysis of the compound into non-toxic phosphonate bound to the surface of the material. In fact, ZnO and CuO nanocrystalline particles have been successfully applied as a coating on cotton fabrics using a sonochemical process (Abramov *et al.*, 2009). A strong immobilization was obtained as no change in nanoparticle concentration in the fabric was observed after twenty washing cycles. The CuO coated fabric demonstrated some biocidal activity with *E.coli*, with a 2–3 log reduction in cell number after 120 min of incubation.

Polyoxometalate $H_5PV_2Mo_{10}O_{40}$ nanoparticles were also used to produce a self-decontaminating membrane (Wu *et al.*, 2009). The nanoparticles were added to a PVA/polyethyleneimine blend before polymerization. The resulting membrane displayed satisfactory efficiency against both 2-chloroethyl-ethyl sulfide, a mustard analog, and various species of Gram-positive and Gram-negative bacteria. The membrane also showed some water vapor permeability.

Silver salt nanocrystals are another type of nano-object with a large potential for self-decontaminating barriers as they exhibit a high antibacterial performance while maintaining a wide-range of biocidal capacities (Tessier *et al.*, 2005). A uniform distribution of crystals was obtained by application of a silver salt colloidal solution on various fabrics (see Fig. 5.6).



5.6 Scanning electron microscopy image of silver salt crystal particles applied on a nylon/spandex fabric. (Sample graciously provided by Medifit Marketing Inc., St-Hyacinthe, QC, Canada.)

The antimicrobial activity was further enhanced, due to the antimicrobial surfactant added to prevent coagulation and favor small crystal precipitation. Silver salt nanocrystals were also encapsulated in a polymer and applied as a coating on cotton and polyester microfibrous fabrics (Tessier *et al*., 2006). A kill rate of *Clostridium difficile* bacteria of 99.99% was achieved within a minute. In addition, the fabric silver salt treatment was demonstrated to be non-toxic to human health.

Nanotubes have also experienced some interesting development for self-decontamination. For example, $V_{1.02}O_{2.98}$ nanotubes were synthesized from vanadium pentoxide (Mahato *et al*., 2009b). Needle-like structures were obtained with an outer diameter between 50 and 150 nm, an inner diameter between 30 and 100 nm, and a length between 1 and 3 μm. Degradation of sulfur mustard and sarin was observed to proceed as a result of oxidation and hydrolysis, leading to non-toxic reaction products, sulfur mustard sulphoxide and isopropyl methyl phosphonic acid. Half-life values were measured to be between 6 and 7h. Titanium dioxide nanotubes efficiency against sulfur mustard was increased by modification with silver ions (Prasad *et al*., 2009). An accelerated hydrolysis of the toxic compound was observed, with half-life values decreasing from 5.99 to 3.8h compared to non-modified nanotubes.

Progress has also recently been made towards the production of ceramic nanofibers by electrospinning (Sundarrajan *et al*., 2010). This technique has the great advantages of being simple, versatile and relatively inexpensive, and allows the formation of continuous nanofibers. Zinc titanate and MgO nanofibers were obtained by combining sol–gel and electrospinning techniques. Zinc titanate displayed satisfactory efficiency against paraoxon. Finally, nano-objects, thanks to their high surface area, may also be choice candidates to serve as supports for self-decontaminating compounds. For example, silica nanoparticles have been impregnated with chemicals active against sulfur mustard and other nerve and blister agents (Singh *et al*., 2009; Saxena *et al*., 2011). The mechanism of action involved hydrolysis, dehydrohalogenation and oxidation.

Photocatalytic decomposition can also be used as a self-decontamination process against chemical and biological hazards. In particular, several types of metal oxide nanoparticles have demonstrated some photocatalytic activity against toxic chemicals, bacteria, viruses and other organic compounds (Sundarrajan *et al*., 2010). For example, TiO_2, in combination with exposure to UV light, was able to degrade 2-chloroethyl sulfide (mustard) in liquid and gas phase, as well as a series of chemical warfare agents such as diethyl sulfide, dimethyl methyl phosphonate, diethyl phosphoramidate, pinacolylmethylphosphonate and butylaminoethanethiol. The reaction proceeds through preferential adsorption of the compound on TiO_2 sites followed by photocatalytic oxidation. Immobilized TiO_2 nanoparticles also displayed

self-decontamination capabilities for pesticides such as lindane, methyl parathion and dichlorvos, under UV irradiation (Senthilnathan and Philip, 2009). Full decontamination was obtained within one hour and no significant change in reaction rate was observed for three successive re-uses. The UV-activated decomposition of ammonia gas by TiO_2 nanoparticles was also investigated (Dong *et al*., 2006). The TiO_2 nanoparticles were applied on cotton and cotton/polyester fabrics using an aqueous suspension with a silicone softener. A level of ammonia gas decomposition of 100% was achieved within 10 minutes of exposure for the cotton fabric.

The semi-conductor compound ZnO can also play the role of photocatalyst and its efficiency as anti-bacterial agent is well known (Muñoz-Bonilla and Fernandez-Garcia, 2012). ZnO nanoparticles have been successfully incorporated into several polymers such as nylon 6 and low density polyethylene, with good anti-microbial properties. ZnO-containing nanocomposites fibers were produced by electrospinning with polyurethane, and applied as a coating over cotton fabrics, providing them with an anti-microbial function.

Other metal oxides have also demonstrated interesting capabilities. For example, WO_3-modified titanate nanotubes were produced and applied by dripping, spray deposition and layer-by-layer deposition on cotton/polyamide textiles (Grandcolas *et al*., 2011). Only the layer-by-layer technique provided a homogeneous and strongly anchored deposit. Photocatalytic decomposition of yperite blister agent and dimethyl methylphosphonate (DMMP) neurotoxic simulant was achieved under solar light in short times, with, for example, a complete disappearance of DMMP after 7 minutes of exposure.

A totally different type of strategy is based on the formation of peroxides by the reduction of oxygen by photogenerated hydroxyl radicals (Little, 2011). These radicals can be obtained with sulfonated poly(ether ether ketone)/poly(vinyl alcohol) (SPEEK/PVA) blends. A constant production rate of peroxide is thought to be achievable with SPEEK/PVA fibers as their high surface area would allow the availability of a large enough concentration in oxygen for the reaction to proceed.

A final example of a light-activated decontamination process relies on singlet oxygen. This very reactive chemical intermediate reacts with a wide variety of chemical and biological species (Brewer *et al*., 2010). It can be photochemically generated by dyes such as Rose Bengal which converts molecular oxygen into singlet oxygen upon excitation by illumination. Tests were carried out with Rose Bengal dyed nylon fabrics exposed to fluorescent light and daylight. Destruction of 2-(phenylthio)ethanol (a model for sulfur mustard) and *E. coli* bacteria was achieved in, respectively, 1 hour and 30 minutes. Repeated irradiation tests showed a need for improved stability. In addition, the sulfide reaction products included a

small quantity of sulfone, which is as toxic as sulfur mustard. Aluminum phthalocyanine is another photosensitive dye which has been evaluated for the development of self-decontaminating textiles (Cole, 2011). It showed a 50 to 74% conversion rate in a series of chemical warfare agents after two hours of irradiation with a solar simulation lamp. The treated fabrics also displayed a wide-range anti-bacterial activity, and a high reduction (>log5) in Gram-positive and Gram-negative bacteria within 5 minutes.

Various techniques have been investigated for incorporating self-decontaminating functions into chemical and biological barriers. Active compounds may, for example, be added as a finish or enter in the membrane fabrication process (Obendorf, 2010). For the manufacture of fibrous membranes, electrospinning offers the great advantage of producing high surface area fibers in a relative simple and flexible way. Functionalization may be performed pre- or post-spinning (Daels *et al.*, 2011). In the first case, the active compound is added to the spinning solution or melt, and its reactivity is enhanced by the high number of active sites and the low diffusion path. For post-spinning functionalization, the high surface area of the fibers translates into a high density of anchoring sites for the active compound. To that extent, nanofibers represent a great opportunity for maximising the reactivity of the self-decontaminating barriers (Sundarrajan *et al.*, 2010).

In an attempt to overcome the weakness of the pre-spinning functionalization linked to the low ratio of the active compound availed at the fiber surface while still benefiting from a one-step technique, the electrospraying and electrospinning processes have been combined. An electrospun–electrosprayed membrane was produced with polysulfone and TiO_2 nanoparticles. Another strategy consisted in alternating layers of electrospun polymer and electrosprayed nanoparticles. These membranes display a reduced air flow resistance and an improved reactivity compared with other manufacturing techniques.

As an alternative to the incorporation of active species in a matrix or their binding at the surface of a host structure, the use of synthetic anti-microbial polymers presents several advantages (Muñoz-Bonilla and Fernandez-Garcia, 2012). Indeed, they are generally less toxic and irritant than low molecular weight anti-bacterial agents, and display stronger and prolonged anti-microbial activity. They include polymers with quaternary nitrogen atoms, polymers containing guanidine, polymers mimicking natural peptides, halogen polymers, polymers with phenol and benzoic acid groups, and organometallic polymers. These anti-microbial polymers operate by destroying the bacteria cell wall.

Some techniques have also been developed to prepare multifunctional materials. One solution consists of a multilayer system in which each porous layer is surface-modified with a different reactive compound (Li, 2009). It may, for example, include a basic layer, an acidic layer and an oxidative

layer. The whole system is breathable and can further be chemically linked to a fabric for support. Another approach is based on layer-by-layer electrostatic assembly (Chen, 2009). This technique has allowed the controlled deposition of a reaction polyanion, used for the decomposition of organophosphate nerve agents, and an antimicrobial polycation on electrospun fiber mats. More recently, the technique was successfully proved to asymmetrically functionalize electrospun fibers with multiple coatings based on weak and strong polyelectrolytes, dendritic compounds and nanoparticles (Krogman, 2009). This opens the door for easy custom-building of chemical and biological breathable barriers that can adapt to new, emerging threats.

5.4 Advantages and challenges of responsive and self-decontaminating barriers

Responsive and self-decontaminating barriers offer numerous advantages for protective clothing against chemical and biological hazards. They can provide less bulky and more breathable membranes, which reduces the risk of heat stress and increases the ease of movement of the wearer. In addition, since multifunctional treatments can be included in a single barrier, protection can be provided against a much larger range of threats at the same time. The protection offered may also adapt to the risks encountered. This allows the wearer to be always fully protected while not carrying the burden of an overprotection when not necessary. Such need is becoming more and more striking as emergency response teams, for example, are faced with an increasing variety of situations, most often without proper information about all the dangers involved. On the other hand, degradation of toxic components upon contact can prevent the risk of secondary contamination; for example, of support team members and nearby unprotected people. Such functionality is crucial because signs of contamination are not always easy to detect with the naked eye, let alone on dust- or ash-covered clothing, and as operation zones shift more and more to urban areas. Finally, the technologies associated with the development of these responsive and self-decontaminating barriers are generally very versatile, which is a large advantage as new threats are constantly emerging and need to be taken care of.

However, although the advantages of these responsive and self-decontaminating barriers are appealing, several challenges remain. First, some technological difficulties still need to be solved. For example, the incorporation of electric sensors and actuators into clothing is limited by problems with interconnects and the need for contactless components, requirements in terms of deformability, mechanical resistance, and friction associated with the manufacturing process, as well as issues with low signal amplitude,

reliability, power generation and transmission, electronic shielding, stability in service, and durability in use and as a result of maintenance (Van Langenhove *et al*., 2005; Linz, 2007; Cherenack *et al*., 2010). The stability of active chemicals used for self-decontamination is also an issue (Brewer *et al*., 2010; Rory, 2007).

A second limiting factor is the response time of these solutions. Indeed, contamination by chemical and biological agents generally takes place at a very rapid pace (Rory *et al*., 2007). However, response to stimuli relying on the diffusion of chemical species through polymer systems is generally a slow process (Roy, 2010). Kinetics obtained with self-decontaminating agents is also often measured in hours; at the very best in minutes (Sundarrajan *et al*., 2010; Muñoz-Bonilla and Fernandez-Garcia, 2012). Only a few technologies currently display response times of a minute or less. This is, for example, the case with nano silver salt crystals (Tessier *et al*., 2006), polymer brushes (Minko and Motornov, 2007) and SMM hydrogels (Van Langenhove *et al*., 2005).

A third important question is the need for an absence of impact on health and the environment of the responsive and self-decontaminating membrane active compounds and their degradation products. One part of the difficulty is to lower the toxicity to human beings while maintaining a high level of reactivity towards toxic chemical and biological agents. The use of synthetic anti-microbial polymers, as well as encapsulation, may provide some solutions to this problem (Muñoz-Bonilla and Fernandez-Garcia, 2012). To prevent leaching of the active compounds into the environment, a strong tethering to the membrane structure can be provided by chemical crosslinking (Wynne *et al*., 2011).

Another important challenge is durability in use and during maintenance. Indeed, wear and cleaning treatments may induce a progressive loss in performance (Van Langenhove *et al*., 2005). It is therefore crucial to submit developed solutions to test programs simulating service use and maintenance treatments to verify their durability.

A fifth issue deals with test methods. Indeed, dedicated protocols and requirements need to be developed for responsive and self-decontaminating protective clothing. For example, a new test method is currently in elaboration by the ASTM F23.30 committee on personal protective clothing and equipment for measuring the effectiveness of self-decontaminating surfaces for protective clothing materials (Cole, 2011).

Integration is also an important difficulty to be tackled. It involves the interaction of different active compounds in multifunctional membranes and in layered systems, as well as the problems associated with interfaces with the rest of the protective equipment components. And finally, adaptive membranes represent a major challenge, since they require reversible changes to be modulated by the intensity of the stimuli.

5.5 Applications of responsive and self-decontaminating barriers

A set of applications for which responsive and self-decontaminating barriers have raised a lot of interest deals with the medical sector. Requirements for medical personnel uniforms include anti-microbial and liquid-repellent properties to prevent the spreading of bacteria between patients and health-care workers, and breathability (Liu, 2010). A proposed solution involves combining reversible swelling and self-decontamination in a single membrane (Liu, 2009). It is obtained by grafting a self-decontaminating and reversibly swellable polymer to a porous substrate. When in contact with infectious fluids, the polymer swells and blocks the pores of the substrate while simultaneously destroying the bacteria. In addition, a product has been developed by Ahlstrom Corp. to provide an increasing breathability as the wearer's temperature rises (Rodie, 2005). It is based on a temperature-responsive, breathable, monolithic film, sandwiched between two layers of spunbond microfibrous polypropylene and is marketed as a medical gown for protection against infectious fluid-borne viruses.

Another area where some progress has been made towards the development of responsive and self-decontaminating barriers is the military. Current systems inherited from the Cold War era suffer from an excess of thickness and weight, are task restrictive, and offer insufficient permeability (Duncan, 2006). They result in a high burden for the wearer, non-optimized protection, moisture and heat management problems and integration issues among others. The ideal solution would be multi-functional protective clothing with self-decontamination capabilities (Sun *et al.*, 2008). It would rapidly destroy/detoxify a large variety of chemical and biological agents upon contact, be breathable and remain comfortable to wear for long periods of time, even under high workloads, be safe for humans and the environment, be resistant to long storage, service wear and maintenance, and be reusable with the possibility of subsequent easily restored chemical and biological activity.

Several projects are currently in progress to reach these goals (Galloway, 2007). They involve a nanowire mesh fabric at NanoSys; a multi-layered self-decontaminating system at GE/Foster-Miller; a laminated membrane based on polyurethane, Nafion, chitosan and Nomex at DuPont; an integrated system comprising a biocide and water repellent outershell, sandwiched reactive nanoparticles, a reactive permselective film and a reactive sorptive liner at Natick; chemical agent sensors based on conductive polymers at TDA Research; and self-detoxifying materials based on N-halamine at Gentex.

Emergency first-responders are also subjected to a variety of chemical, biological, radiological and nuclear (CBRN) threats, which comprise nerve

and blister agents, toxic industrial chemicals and materials, bacteria, viruses and biological toxins, as well as radiological and nuclear materials (Fatah *et al.*, 2007). These hazards may be encountered during contaminated-site survey, emergency rescue, hazard mitigation, monitoring or supervision activities, and decontamination operations. Protective ensembles can be totally encapsulating if they enclose the respirator, or non-encapsulating. The National Fire Protection Agency (NFPA) standards define three categories of protective clothing: Class 1 corresponds to situations where the nature of the chemical or biological threat, its concentration and its toxicity are unknown, and requires total encapsulation; Class 2 ensembles should be worn when the hazard concentration is at or above the immediately-dangerous-to-life-or-health (IDLH) level, and involves limited exposure to gases, vapors, liquid droplets and splashes; and Class 3 refers to cases when concentration of the hazard is at or below the short-term exposure limit (STEL) and skin contact is not likely.

Current technologies for emergency first-responders' clothing generally rely either on impermeable materials or on breathable, selective permeable membranes combined with an active charcoal liner. However, these low or non-breathable protective clothing systems are associated with a higher risk of heat stress resulting from an increased body temperature at high environmental temperatures, high levels of humidity, and high workloads for prolonged periods of time. Current solutions to this problem are based on active or passive cooling systems, which increase weight and lead to limited mobility. New products with responsive and self-decontaminating barriers are thus deeply needed.

Another type of activity on which the development of responsive and self-decontaminating protective clothing would have a strong impact is associated with industrial chemical workers. Four categories of chemical barriers may be distinguished (Stull, 2005): *Permeation-resistant* ones prevent any contact with gases/vapors, liquids and particles of specific chemicals; *Vapor penetration-resistant* ones block atmospheric vapors and gases; *Liquid penetration-resistant* ones limit contact with liquids; and *particle penetration-resistant* barriers protect only from particles.

Currently available protective clothing products for industrial chemical workers are based on seven types of materials/structures: textiles, unsupported rubbers and plastics, microporous film fabrics, absorbent-based fabrics, coated fabrics, plastic laminates, and combination or specialized materials. They display various levels of protection against various types and forms of chemicals. They also have to fulfil other requirements; for example, mechanical strength, resistance to physical hazards and durability as well as ergonomic properties such as biocompatibility, thermal insulation, breathability, mobility, and ease of donning and doffing. However, achieving sufficient chemical protection often involves reduced functionality and comfort.

A final example of a domain where responsive and self-decontaminating barriers make a difference, deals with sport protective clothing. Sport garments should provide protection from the environment; for example, rain, sun, wind, impact from objects, as well as comfort and thermoregulation (Popa *et al.*, 2009). They should not, in any case, impair the range of motion and the flexibility, and may even contribute to the enhancement of the user's performance. In terms of modulated breathability, temperature-responsive polymers with a lower critical solution temperature in the physiological range offer interesting possibilities as they become more hydrophobic above that value (Crespy and Rossi, 2007). They include, for example, poly(vinyl ethers), poly(N-substituted acrylamides) and poly(n-vinyl caprolactam). A commercial thermo-responsive breathable membrane used in sport clothing and marketed as Diaplex has also been developed by Mitsubishi Heavy Industries (SMP Technologies Inc, 2010). It is based on shape memory polyurethane and can be laminated on various types to textiles to be used as a waterproof, windproof, yet breathable, membrane. Increased water vapor transmission rate occurs as temperature rises thanks to thermally-activated micro-Brownian motion which allows the free volume formation.

5.6 Conclusion and future trends

Much progress has already been made towards the development of responsive and self-decontaminating barrier membranes. With innovative technologies based on nanomaterials, electrospinning, graft polymerization or N-halamine compounds for example, promising solutions exist for providing better protective clothing against chemical and biological hazards.

As far as the future goes, the development of smart solutions for protective clothing is relying more and more on the idea of combining different materials at the particle, fiber and fabric/film levels (Gomes, 2009). To that extent, nanomaterials provide numerous opportunities. Available as nanofibers or nanocomposite fibers for example (Brown and Steven, 2007), they can be easily incorporated into the clothing membrane thanks to their small size. There, they can act as sensor or actuator (Devaux, 2007). Used as nanocoatings or nanofilms, they improve the resistance to permeation by increasing the diffusion path, with a potential for tailoring the system response to the needs (Duncan, 2006). In addition, nanofibrous filters and nanowebs benefit from a low density, a small pore size and a good interconnectivity of the pore structure (Barhate and Ramakrishna, 2007), and can be easily produced by electrospinning. And, above all, nanomaterials display a very high effective surface area, which makes them choice candidates for the incorporation of active chemistry and functionalities. As a result, only a very small quantity of the nano-sized active compound, generally less than

5 wt.%, is necessary to make the whole system efficient (Muñoz-Bonilla and Fernandez-Garcia, 2012).

In terms of processes, the trend goes towards cheaper and faster methods, as well as localized action. Electrospinning appears an ideal technique for producing fibers in nano, meso and microscale. Indeed, it is a simple and easily up-scalable technology (Popa *et al.*, 2009). In addition, it can accommodate a large variety of organic and inorganic materials, which makes it a very versatile technique. Integration of manufacturing processes is another part of the solution. For example, electrospinning has been combined with electrospraying so that nanofibers are produced and simultaneously coated with nanoparticles (Sundarrajan *et al.*, 2010). For its part, reactive extrusion involves fiber melt extrusion and *in-situ* graft polymerization functionalization (Sun, 2006). Grafting of polymer brushes offers a wide range of possibilities of surface and pore chemical modification (Olivier *et al.*, 2012). This technique is also very versatile since it applies to a wide range of polymers.

The trend for functionality is to design multifunctional systems with a wide range of action and a reduced toxicity. For example, full spectrum decontamination can be obtained by combining chemicals with complementary reactivity in different layers of the clothing system, or even within a unique membrane (Schreuder-Gibson, 2009). It may also involve combining organic and inorganic anti-microbial agents (Muñoz-Bonilla and Fernandez-Garcia, 2012). Different approaches may also be pooled; for example, reversible swelling for blocking toxic agent entry and self-decontamination (Liu, 2009). Reduced toxicity can be obtained, for example, with encapsulation or by molecular engineering (Muñoz-Bonilla and Fernandez-Garcia, 2012).

For clothing systems, the tendency is towards integration. It involves the various layers of the clothing piece – the shell, the barrier, and the liner – for optimized performance (Schreuder-Gibson, 2009). It also deals with the compatibility between the different components of the protective ensemble. Indeed, interfaces between the hood and mask, the jacket and gloves, and the trousers and boots have been identified as weak points for gas and vapor penetration (Truong and Wilusz, 2005). An elasticized carbon-based closure system is currently in development at Natick as a solution for this issue (Seessel, 2005). In addition, sufficient overlap between clothing components is required to allow extension and bending movements without breaching the protection (Stull, 2005). It also implies that all the components of an ensemble must be initially designed to fit together rather than being assembled *a posteriori*.

Finally, the ultimate trend will be towards adaptive barriers that will rapidly adjust to their environment and to the intensity of the threat, in a reversible manner. They will be, for example, breathable in a non-hazardous

environment but become semipermeable or impermeable when a hazard is detected. They will also destroy toxic agents upon contact. These adaptive barriers will be the key for optimal protection, functionality and comfort as they will fine-tune their properties to the encountered conditions.

5.7 Sources of further information and advice

- Center for Bio/Molecular Science & Engineering, Naval Research Laboratory, USA: nrlbio.nrl.navy.mil.
- Centexbel, Belgium: www.centexbel.be.
- Centre for Nanotechnology and Smart Materials, Portugal: www.centi.pt.
- Chemical and Biological Defence Section, Defence R&D Canada, Canada: www.suffield.drdc-rddc.gc.ca.
- Chemical Systems Research Division, Chung- Shan Institute of Science and Technology, Taiwan: www.csistdup.org.tw/english.
- College of Textiles, North Carolina State University, USA: www.tx.ncsu.edu.
- CTT Group, Center for Textile Technologies, Canada: www.groupectt-group.com.
- Department of Chemical and Biological Engineering, Drexel University, USA: www.chemeng.drexel.edu.
- Department of Chemical Engineering, Massachusetts Institute of Technology, USA: web.mit.edu/cheme.
- Department of Chemistry and Biochemistry, Auburn University, USA: www.auburn.edu/cosam/departments/chemistry.
- Department of Fiber Science & Apparel Design, Cornell University, USA: www.human.cornell.edu/fsad.
- Department of Organic Materials and Textile System Engineering, Chungnam National University, South Korea: plus.cnu.ac.kr/english.
- Department of Textile Sciences, University of Manitoba, Canada: umanitoba.ca/faculties/human_ecology/departments/ts.
- Division of Textiles and Clothing, University of California, USA: textiles.ucdavis.edu.
- Department of Textiles, Ghent University, Belgium: textiles.UGent.be.
- GEMTEX, Ecole Nationale Supérieure des Arts et Industries Textiles, France: www.ensait.fr/Espace-neutre/Recherche/Le-GEMTEX.
- Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne, Swizerland: isic.epfl.ch.
- Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Russia: www.igic.ru.
- Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, University of Strasbourg, France: lmspc.alsace.cnrs.fr.

- Laboratory for Protection and Physiology, EMPA, Swizerland: www.empa.ch.
- Nanoscience and Nanotechnology Initiative, National University of Singapore, Singapore: www.nusnni.nus.edu.sg.
- National Textile Center, USA: www.ntcresearch.org.
- School of Materials, University of Manchester, UK: www.materials.manchester.ac.uk.
- State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, College of Environmental Science and Engineering, Nankai University, China: env.nankai.edu.cn.
- U.S. Army Edgewood Chemical and Biological Center, USA: www.ecbc.army.mil.
- U.S. Army Natick Soldier Research, Development, and Engineering Center, USA: nsrdec.natick.army.mil.

5.8 Acknowledgments

The author would like to thank Ms Maud Leblanc for helping with the preparation of the manuscript, Mr Ludwig Vinches for the scanning electron microscopy imaging and Mr Bernard Rose from Medifit Marketing Inc. (St-Hyacinthe QC Canada) for providing the silver salt crystal coated nylon/spandex fabric sample.

5.9 References

Abramov, O. V., Gedanken, A., Koltypin, Y., Perkas, N., Perelshtein, I., Joyce, E. and Mason, T. J. 2009. Pilot scale sonochemical coating of nanoparticles onto textiles to produce biocidal fabrics. *Surface and Coatings Technology*, 204, 718–722.

ASTM 1999. *Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact*. ASTM F 739-99a. American Society for Testing and Materials.

ASTM 2003. *Standard Test Method for Resistance of Materials Used in Protective Clothing to Penetration by Blood-borne Pathogens using Phi-X174 Bacteriophage Penetration as a Test System*. ASTM F 1671–03. American Society for Testing and Materials.

Barhate, R. S. and Ramakrishna, S. 2007. Nanofibrous filtering media: filtration problems and solutions from tiny materials. *Journal of Membrane Science*, 296, 1–8.

Bealer Rodie, J. 2006. *Enzyme Therapy* [Online]. Available: http://www.textileworld.com [Accessed 28 Sept 2006].

Begriche, A. and Lachapelle, D. 2010. Intelligent textiles for protection – Overview of technologies. *Soldier Systems Technology Roadmap – Soldier Survivability/Sustainability/Mobility Workshop*, May 13th. Ottawa, ON: Government of Canada.

Brewer, S. A., Artiles, C. P., Taylor, J. A. and Dennis, M. 2010. Photosensitive dyes and self-detoxifying textiles: degradation products and dye durability. *Applied Surface Science*, 256, 1908–12.

Brock, D., Lee, W., Segalman, D. and Witkowski, W. 1994. A dynamic model of a linear actuator based on polymer hydrogel. *Journal of Intelligent Materials and Structures*, 5, 764–771.

Bromberg, L., Schreuder-Gibson, H., Creasy, W. R., McGarvey, D. J., Fry, R. A. and Hatton, T. A. 2009. Degradation of chemical warfare agents by reactive polymers. *Industrial and Engineering Chemistry Research*, 48, 1650–1659.

Brown, P. J. and Stevens, K. 2007. *Nanofibers and Nanotechnology in Textiles*, Boca Raton, Boston, FL, USA: CRC Press LLC; Cambridge, UK: Woodhead Publishing Ltd.

Brown, P. J. 2001. Hollow fibre membranes for gas separation. In: Tao, X. (ed.) *Smart Fibers, Fabrics and Clothing*. Boca Raton, FL, USA: CRC Press LLC; Cambridge, UK: Woodhead Publishing Ltd.

Brun, E., De Beeck, R. O., Van Herpe, S., Isotalo, L., Laamanen, I., Blotièere, C., Mur, J.-M., Orthen, B., Wagner, E., Flaspoler, E., Reinert, D., Galwas, M., Posniak, M., Carreras, E., Guardino, X. and Solans, X. 2009. *Expert Forecast on Emerging Chemical Risks Related to Occupational Safety and Health*. European Agency for Safety and Health at Work.

Burtovyy, O. 2008. *Synthesis and Characterization of Macromolecular Layers Grafted to Polymer Surfaces*. Ph.D. Dissertation, Clemson University, Clemson, SC.

Butler, I. 2000. *Filtration Technology Handbook*, Cary, NC: INDA Publications.

Carson, P. and Mumford, C. 2002. *Hazardous Chemical Handbook*, Oxford, UK: Butterworth-Heinemann.

Chen, H., Palmese, G. R. and Elabd, Y. A. 2005. Polyester–polyelectrolyte nanocomposite membranes as breathable and responsive barriers. *2005 AIChE Annual Meeting and Fall Showcase*, October 30 – November 4, Cincinnati, OH, USA: American Institute of Chemical Engineers, 4886.

Chen, L. 2009. *Next Generation of Electrospun Textiles for Chemical and Biological Protection and Air Filtration*. Ph.D. dissertation. Massachusetts Institute of Technology, Cambridge, MA.

Cherenack, K., Zysset, C., Kinkeldei, T., Münzenrieder, N. and Tröster, G. 2010. Woven electronic fibers with sensing and display functions for smart textiles. *Advanced Materials*, 22, 5178–5182.

Cireli, A., Mutlu, M., Kutlu, B., Onar, N., Kayatekin, I. and Celik, E. 2006. Sol–gel coatings of plasma modified polypropylene fabric for gas defence. *Proceedings of the 3rd European Conference on Protective Clothing* and *Nokobetef 8*, 10–12 May 2006, Gdynia, Poland.

Cole, J. 2011. Self-decontaminating technologies for use in chemical protective clothing. *Ninth Symposium on Performance of Protective Clothing and Equipment: Emerging Issues and Technologies*. Anaheim, CA: ASTM Committee F23 on Personal Protective Clothing and Equipment.

Comyn, J. 1985. *Polymer Permeability*, Essex, UK: Elsevier Applied Science.

Crespy, D. and Rossi, R. M. 2007. Temperature-responsive polymers with LCST in the physiological range and their applications in textiles. *Polymer International*, 56, 1461–8.

Daels, N., De Vrieze, S., Sampers, I., Decostere, B., Westbroek, P., Dumoulin, A., Dejans, P., De Clerck, K. and Van Hulle, S. W. H. 2011. Potential of a functionalised

nanofiber microfiltration membrane as an antibacterial water filter. *Desalination*, 275, 285–290. DOI: 10.1016/j.desal.2011.03.012.

David, M. 2011. Polymeric ionic liquids: broadening the properties and applications of polyelectrolytes. *Progress in Polymer Science*, 36, 1629–1648.

Devaux, E. 2007. Applications des nanotechnologies aux vêtements de protection personnels. *Expo HighTex 2007*. Montréal, Canada.

Dolez, P. I. and Vu-Khanh, T. 2009. Recent developments and needs in materials used for personal protective equipment and their testing. *International Journal of Occupational Safety and Ergonomics*, 15, 347–362.

Dolez, P., Soulati, K., Gauvin, C., Lara, J. and Vu-Khanh, T. 2010. *Information Document for Selecting Gloves for Protection against Mechanical Hazards*. Montréal QC Canada: Institut de Recherche Robert-Sauvé en Santé et en Sécurité du Travail.

Dong, Y., Bai, Z., Zhang, L., Liu, R. and Zhu, T. 2006. Finishing of cotton fabrics with aqueous nano-titanium dioxide dispersion and the decomposition of gaseous ammonia by ultraviolet irradiation. *Journal of Applied Polymer Science*, 99, 286–291.

Du, H. and Zhang, J. 2010. Solvent induced shape recovery of shape memory polymer based on chemically cross-linked poly(vinyl alcohol). *Soft Matter*, 6, 3370–3376.

Duncan, S. 2006. *Presentation CB protection for defence* [Online]. Defence Research and Development Canada, www.dtic.mil/ndia/2006cbip/duncan.pdf

DuPont 2005. *Tyvek® and Tychem® Protective Clothing: Technical Handbook*. DuPont Personal Protection.

DuPont 2007. *DuPont Hybrid Membrane Technology*. DuPont Personal Protection.

Elabd, Y. A. and Palmese, G. R. 2007. *Filled Nanoporous Polymer Membrane Composites for Protective Clothing and Methods for Making Them*. US patent application PCT/US2007/069658.

El-Sherif, M. A., Yuan, J. M. and Macdiarmid, A. 2000. Fiber optic sensors and smart fabrics. *Journal of Intelligent Material Systems and Structures*, 11, 407–414.

Fang, Y., Guo-Dong, F., Junpeng, Z., En-Tang, K. and Koon Gee, N. 2008. Antibacterial effect of surface-functionalized polypropylene hollow fiber membrane from surface-initiated atom transfer radical polymerization. *Journal of Membrane Science*, 319, 149–57.

Fatah, A. A., Arcilesi, R. D., Charpentier, L., Lattin, C. H., Mundinger, J., Tassinari, T. and Richardson, A. 2007. *Guide for the Selection of Personal Protective Equipment for Emergency First Responders*. U.S. Department of Homeland Security.

Feng, J. and MacDiarmid, A. G. 1999. Sensors using octaaniline for volatile organic compounds. *Synthetic Metals*, 102, 1304–1305.

Fenglong, J., Yong, Z., Jinlian, H., Yan, L., Lap-Yan, Y. and Guangdou, Y. 2006. Smart polymer fibers with shape memory effect. *Smart Materials and Structures*, 15, 1547–54.

Fulmer, P. A., Lundin, J. G. and Wynne, J. H. 2010. Development of antimicrobial peptides (AMPs) for use in self-decontaminating coatings. *ACS Applied Materials and Interfaces*, 2, 1266–1270.

Galloway, D. 2007. Challenges and direction in chemical biological defense. *NDIA Conference*. Arlington, VA.

Gibson, P. W. and Schreuder-Gibson, H. 2009. Influence of hydration state on permeation testing and vapor transport properties of protective clothing layers. *Journal of Engineering Fibers and Fabrics*, 4, 11–20.

Gomes, J. 2009. Novel technologies for the development of new and optimized smart materials. *TechtextilAvantex Symposium*. Frankfurt, Germany.

Gowayed, Y., Buschle-Diller, G., Livant, P. and Luzinov, I. 2006. Efficient biological–chemical protective materials. *National Textile Center Annual Report*. Blue Bell, PA.

Grafe, T. and Graham, K. 2002. Polymeric nanofibers and nanofiber webs: a new class of nonwovens. *International Nonwovens Technical Conference*, 24–26 September 2002 Atlanta (Georgia). 377.

Grandcolas, M., Sinault, L., Mosset, F., Louvet, A., Keller, N. and Keller, V. 2011. Self-decontaminating layer-by-layer functionalized textiles based on WO3-modified titanate nanotubes. Application to the solar photocatalytic removal of chemical warfare agents. *Applied Catalysis A: General*, 391, 455–467.

Guillen, G. R. and Hoek, E. M. V. 2010. *Development and Testing of 'Smart' Nanofiltration Membranes*. NWRI Final Project Report. Los Angeles, CA: Department of Civil & Environmental Engineering, University of California.

Hirai, T., Zheng, J., Watanabe, M. and Shirai, H. 2001. Electrically active polymer materials – application of non-ionic polymer gel and elastomers for artificial muscles. In: Tao, X. (ed.) *Smart Fibres, Fabrics and Clothing*. Boca Raton, FL, USA: CRC Press LLC; Cambridge, UK: Woodhead Publishing Ltd.

Hu, J. 2007. *Shape Memory Textiles*. Boca Raton, FL, USA: CRC Press LLC; Cambridge, England: Woodhead Publishing Ltd.

Itoh, T., Matsubara, I., Shin, W., Izu, N. and Nishibori, M. 2008. Preparation of layered organic–inorganic nanohybrid thin films of molybdenum trioxide with polyaniline derivatives for aldehyde gases sensors of several tens ppb level. *Sensors and Actuators: B. Chemical*, 128, 512–20.

Janssen, D. 2008. Responsive materials for PPE. *1st International Conference on Personal Protective Equipment: For More (Than) Safety*. Bruges, Belgium.

Jin, J., Nguyen, V., Gu, W., Lu, X., Elliott, B. J. and Gin, D. L. 2005. Cross-linked lyotropic liquid crystal–butyl rubber composites: promising 'breathable' barrier materials for chemical protection applications. *Chemistry of Materials*, 17, 224–226.

John, M. and Anandjiwala, R. D. 2009. Surface modification and preparation techniques for textile materials. In: WEI, Q. (ed.) *Surface Modification of Textiles*. Cambridge, UK: Woodhead Publishing Ltd.

Keighley, J. H. 1985. Breathable fabrics and comfort in clothing. *Journal of Industrial Textiles*, 15, 89–104.

Kiekens, P., Van Langenhove, L. and hertleer, C. 2004. Smart clothing: A new life. *International Journal of Clothing Science and Technology*, 16, 63–72.

Kim, Y. H. and Sun, G. 2001. Durable antimicrobial finishing of nylon fabrics with acid dyes and a quaternary ammonium salt. *Textile Research Journal*, 71, 318–323.

Kimberly-Clark. *Protective Garments: Comfort that Protects*. [Online] www.kcprofessional.com.

Krogman, K. C. 2009. *Functionalized Multilayer thin Films for Protection Against Acutely Toxic Agents*. Ph.D. dissertation, Massachusetts Institute of Technology, Cambridge, MA .

Lee, Y. M. and Shim, J. K. 2001. Permeation control through stimuli-responsive polymer membrane prepared by plasma and radiation grafting techniques. In: Tao, X. (ed.) *Smart Fibres, Fabrics and Clothing*. Boca Raton, FL, USA: CRC Press LLC; Cambridge, England: Woodhead Publishing Ltd.

Lee, Y. M. and Kim, S. Y. 2001. Stimuli-responsive interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and poly(acrylic acid). In: Tao, X. (ed.) *Smart Fibres, Fabrics and Clothing*. Boca Raton, FL, USA: CRC Press LLC; Cambridge, UK: Woodhead Publishing Ltd.

Leng, J., Lan, X., Liu, Y. and Du, S. 2011. Shape-memory polymers and their composites: Stimulus methods and applications. *Progress in Materials Science*, 56, 1077–1135.

Li, W., Jang, D. M., An, S. Y., Kim, D., Hong, S.-K. and Kim, H. 2011. Polyaniline-chitosan nanocomposite: High performance hydrogen sensor from new principle. *Sensors and Actuators, B: Chemical*, 160, 1020–1025.

Li, X. 2009. *Toward a Breathable Fabric for Protection Against Airborne Toxic Chemicals, and an Olefin-forming Cascade Reaction en route to 2,2′-bi(glycerol)*. Ph. D. dissertation. Auburn University, Auburn, AL.

Lin, C.-Y., Liao, K.-H., Su, C.-F., Kuo, C.-H. and Hsieh, K.-H. 2007. Smart temperature-controlled water vapor permeable polyurethane film. *Journal of Membrane Science*, 299, 91–96.

Linz, T. 2007. Technologies for integrating electronics in textiles. *4th International Avantex Symposium*. Frankfurt/Maine, Germany.

Little, B. K. 2011. *Smart Materials for Advanced Applications: Self-decontaminating Polymers, Photofunctional Composites, and Electroconductive Fibers*. Ph.D. dissertation, Auburn University, Auburn, AL.

Liu, S. and Sun, G. 2006. Durable and regenerable biocidal polymers: acyclic N-halamine cotton cellulose. *Industrial and Engineering Chemistry Research*, 45, 6477–6482.

Liu, S. and Zhou, X. 2002. Suface-crosslinking of a superabsorbent polyacrylate. *International Symposium on Polymer Physics, PP'2002*. Qingdao, China.

Liu, S. 2009. *Protective Barrier Having Self-decontaminating Properties*. European Patent Office, WO 2009127052.

Liu, S. 2010. 'Smart' protective textile: responsive barrier and self-disinfection. *Sustainable Textiles and Medical Protection Conference (STAMP 2010)*. Davis, CA.

Liu, S., Zhao, N. and Rudenja, S. 2010. Surface interpenetrating networks of poly(ethylene terephthalate) and polyamides for effective biocidal properties. *Macromolecular Chemistry and Physics*, 211, 286–296.

Lomax, G. R. 1985. The design of waterproof, water vapour-permeable fabrics. *Journal of Industrial Textiles*, 15, 40–66.

Luzinov, I. 2007. Nanofabrication of thin polymer films. In: Brown, P. J. and Stevens, K. (eds.) *Nanofibers and Nanotechnology in Textiles*. Boca Raton, FL, USA: CRC Press LLC; Cambridge, UK: Woodhead Publishing Ltd.

Mahato, T. H., Prasad, G. K., Singh, B., Acharya, J., Srivastava, A. R. and Vijayaraghavan, R. 2009a. Nanocrystalline zinc oxide for the decontamination of sarin. *Journal of Hazardous Materials*, 165, 928–932.

Mahato, T. H., Prasad, G. K., Singh, B., Srivastava, A. R., Ganesan, K., Acharya, J. and Vijayaraghavan, R. 2009b. Reactions of sulfur mustard and sarin on $V_{1.02}O_{2.98}$ nanotubes. *Journal of Hazardous Materials*, 166, 1545–1549.

Marcandalli, B. and Riccardi, C. 2006. Plasma treatments of fibres and textiles. In: *Plasma Technologies for Textiles*. Cambridge, UK: Woodhead Publishing Ltd.

Meng, Q. and Hu, J. 2008. Self-organizing alignment of carbon nanotube in shape memory segmented fiber prepared by *in situ* polymerization and melt spinning. *Composites Part A: Applied Science and Manufacturing*, 39, 314–321.

Mezzo, L. 2009. Inteltex, intelligent textiles with several sensing properties. *Techtextil Avantex Symposium*. Frankfurt, Germany.

Minko, S. and Motornov, M. 2007. Hybrid polymer nanolayers for surface modification of fibers. In: Brown, P. J. and Stevens, K. (eds.) *Nanofibers and Nanotechnology in Textiles*. Boca Raton, FL, USA: CRC Press LLC; Cambridge, UK: Woodhead Publishing Ltd.

Motornov, M., Sheparovych, R., Lupitskyy, R., MacWilliams, E. and Minko, S. 2007. Responsive colloidal systems: reversible aggregation and fabrication of superhydrophobic surfaces. *Journal of Colloid and Interface Science*, 310, 481–488.

Muñoz-Bonilla, A. and Fernández-García, M. 2012. Polymeric materials with antimicrobial activity. *Progress in Polymer Science*, 37, 281–339. DOI: 10.1016/j.progpolymsci.2011.08.005.

Nguyen, Q. T., Alaoui, O. T., Yang, H. and Mbareck, C. 2010. Dry-cast process for synthetic microporous membranes: physico-chemical analyses through morphological studies. *Journal of Membrane Science*, 358, 13–25.

Obendorf, S. K. 2010. Improving personal protection through novel materials. *AATCC Review*, July/August, 44–50.

Olivier, A., Meyer, F., Raquez, J.-M., Damman, P. and Dubois, P. 2012. Surface-initiated controlled polymerization as a convenient method for designing functional polymer brushes: from self-assembled monolayers to patterned surfaces. *Progress in Polymer Science*, 37, 157–181.

Ong, K. 2006. *Encapsulation of organophosphorous acid anhydrolase (OPAA) in Nanostructured Materials for the Detection and Decontamination of Chemical Warfare Agents*. Ph.D. dissertation, Drexel University, Philadelphia, PA.

Pich, J. 1966. Theory of aerosol filtration by fibrous and membrane filters. In: Davies, C. N. (ed.) *Aerosol Science*. London and New York: Academic Press.

Popa, A.-M., Crespy, D., Weder, M., Bruhwiler, P. and Rossi, R. 2009. Smart materials for sport textiles. *Techtextile Avantex Symposium*. Frankfurt, Germany.

Prasad, G. K., Singh, B., Ganesan, K., Batra, A., Kumeria, T., Gutch, P. K. and Vijayaraghavan, R. 2009. Modified titania nanotubes for decontamination of sulfur mustard. *Journal of Hazardous Materials*, 167, 1192–1197.

Rodie, J. B. 2005. Responsive protection [medical gown fabrics]. *Textile World*, 155, 66.

Rory, J. K. 2007. *Enzyme-based Detoxification of Organophorsphorus Neutrotoxic Pesticides and Chemical Warfare Agents*. Ph.D. dissertation, Texas A&M University.

Roy, D., Cambre, J. N. and Sumerlin, B. S. 2010. Future perspectives and recent advances in stimuli-responsive materials. *Progress in Polymer Science* (Oxford), 35, 278–301.

Russel, A. J., Kaar, J. L. and Berberich, J. A. 2003. Using biotechnology to detect and counteract chemical weapons. *The Bridge – Linking Engineering and Society*, 33, 19–24.

Saxena, A., Srivastava, A. K., Singh, B. and Goyal, A. 2011. Removal of sulfur mustard, sarin and simulants on impregnated silica nanoparticles. *Journal of Hazardous Materials*, 211, 226–232. DOI: 10.1016/j.jhazmat.2011.07.117.

Schreuder-Gibson, H. 2009. New Materials for the integration of protective membranes and fabrics for CB destruction and protection. *Chemical and Biological Defense Science & Technology Conference*. Dallas, TX.

Schreuder-Gibson, H. L., Truong, Q., Walker, J. E., Owens, J. R., Wander, J. D. and Jones Jr., W. E. 2003. Chemical and biological protection and detection in fabrics for protective clothing. *MRS Bulletin*, 28, 574–578.

Scoble, C. 2011. Nonwoven filter media – A look back, trends and future market needs. *Techtextil North America Symposium 2011*. Las Vegas, Nevada.

Seessel, A. 2005. *Breathable, Lightweight, Elasticized Carbon-based Closures for Chemical Warfare Agent Vapor Management*. Absolute Closure Innovations, Inc. U.S. Department of Defence: Small Business Innovation Research (SBIR) award.

Senthilnathan, J. and Philip, L. 2009. Removal of mixed pesticides from drinking water system by photodegradation using suspended and immobilized TiO_2. *Journal of Environmental Science and Health – Part B Pesticides, Food Contaminants, and Agricultural Wastes*, 44, 262–270.

Seo, M.-H., Yuasa, M., Kida, T., Huh, J.-S., Shimanoe, K. and Yamazoe, N. 2009. Gas sensing characteristics and porosity control of nanostructured films composed of TiO_2 nanotubes. *Sensors and Actuators B: Chemical*, 137, 513–520.

Shimotori, T., Nuxoll, E. E., Cussler, E. L. and Arnold, W. A. 2004. A polymer membrane containing FeO as a contaminant barrier. *Environmental Science and Technology*, 38, 2264–2270.

Singh, A. and Dressick, W. J. 2006. Self-decontaminating textiles for protection against chemical and biological toxins. *Techtextile Symposium North America, 2006*. Atlanta, GA. 1800.

Singh, B., Saxena, A., Nigam, A. K., Ganesan, K. and Pandey, P. 2009. Impregnated silica nanoparticles for the reactive removal of sulfur mustard from solutions. *Journal of Hazardous Materials*, 161, 933–940.

Singh, W. P. 2007. *Nanoparticle Modified Textiles for Protective Clothing*. SBIR/STTR Award Information. U.S. Department of Health and Human Services.

SMP TECHNOLOGIES INC. 2010. *Intelligent Material Able to Adjust Itself Accordingly to Ensure the Highest Level of Comfort and Affinity with Human Body* [Online]. Available: http://www2.smptechno.com/tech/pdf/smpvsspresentation100218.pdf.

Son, Y.-A., Kim, B.-S., Ravikumar, K. and Lee, S.-G. 2006. Imparting durable antimicrobial properties to cotton fabrics using quaternary ammonium salts through 4-aminobenzenesulfonic acid–chloro–triazine adduct. *European Polymer Journal*, 42, 3059–3067.

Stull, J. O. 2005. Civilian protection and protection of industrial workers from chemicals. In: Scott, R. A. (ed.) *Textiles for Protection*. Boca Raton, FL: CRC Press.

Stull, J. O. and McManus, R. E. 2005. Evaluation of three chemical protective clothing materials for selected performance properties. *Journal of ASTM International*, 1, 3–14.

Sun, G. 2006. Integrated production of functional fibers and nonwoven fabrics. *National Textile Center Annual Report*. Blue Bell, PA.

Sun, G., Worley, S. D. and Broughton, R. M. J. 2008. Self-decontaminating materials for chemical biological protective clothing. In: Wilusz, E. (ed.) *Military Textiles*. Boca Raton, FL: CRC Press; Cambridge, UK: Woodhead Publishing Ltd.

Sun, L., Huang, W. M., Ding, Z., Zhao, Y., Wang, C. C., Purnawali, H. and Tang, C. 2011. Stimulus-responsive shape memory materials: a review. *Materials and Design*, 33, 577–640.

Sundarrajan, S., Chandrasekaran, A. R. and Ramakrishna, S. 2010. An update on nanomaterial-based textiles for protection and decontamination. *Journal of the American Ceramic Society*, 93, 3955–3975.

Sung Ho, L., Moon Kyoung, J., Sung Hee, K. and Byung Kyu, K. 2007. Shape memory effects of molded flexible polyurethane foam. *Smart Materials and Structures*, 16, 2486–91.

Tan, K. and Obendorf, S. K. 2006. Surface modification of microporous polyurethane membrane with poly(ethylene glycol) to develop a novel membrane. *Journal of Membrane Science*, 274, 150–158.

Tan, K. and Obendorf, S. K. 2007a. Fabrication and evaluation of electrospun nanofibrous antimicrobial nylon 6 membranes. *Journal of Membrane Science*, 305, 287–298.

Tan, K. and Obendorf, S. K. 2007b. Development of an antimicrobial microporous polyurethane membrane. *Journal of Membrane Science*, 289, 199–209.

Tessier, D., Radu, I. and Filteau, M. 2005. Antimicrobial fabrics coated with nano-sized silver salt crystals. *Technical proceedings of the 2005 NSTI Nanotechnology Conference and Trade Show*.

Tessier, D., Radu, I. and Filteau, M. 2006. Antimicrobial, nano-sized silver salt crystals encapsulated in a polymer coating. *Trends in Nanotechnology International Conference*. Grenoble, France, 4–8 September.

Tondu, B., Emirkhanian, R., Mathe, S. and Ricard, A. 2009. A pH-activated artificial muscle using the McKibben-type braided structure. *Sensors and Actuators: A Physical*, 150, 124–30.

Trentacosta, J. D. and Kapur, V. 2009. *Adaptive Membrane Structure with Insertable Protrusions*. US patent application 7,625,624.

Truong, Q. and Wilusz, E. 2005. Chemical and biological protection. In: Scott, R. A. (ed.) *Textiles for Protection*. Boca Raton, FL: CRC Press.

Van Langenhove, L., Puers, R. and Matthys, D. 2005. Intelligent textiles for protection. In: Scott, R. A. (ed.) *Textiles for Protection*. Boca Raton, FL: CRC Press.

Vigo, T. L. and Thibodeaux, D. P. 2001. Cross-linked polyol fibrous substrates as multifunctional and multi-use intelligent materials. In: Tao, X. (ed.) *Smart Fibres, Fabrics and Clothing*. Boca Raton, FL, USA: CRC Press LLC; Cambridge, UK: Woodhead Publishing Ltd.

W.L. Gore and Associates. 2011. Gore® Chempak® selectively permeable fabric selected for another CBRN suit [Online]. Available: http://www.gore.com/en_xx/news/xrtsuit.html 2011.

Wales, D. 2002. Evaluating barriers for protection against biological hazards. *Technical Textiles International*, 11, 13–16.

Wang, H.-S., Fu, G.-D. and Li, X.-S. 2009. Functional polymeric nanofibers from electrospinning. *Recent Patents on Nanotechnology*, 3, 21–31.

Wu, K. H., Yu, P. Y., Yang, C. C., Wang, G. P. and Chao, C. M. 2009. Preparation and characterization of polyoxometalate-modified poly(vinyl alcohol)/

polyethyleneimine hybrids as a chemical and biological self-detoxifying material. *Polymer Degradation and Stability*, 94, 1411–1418.

Wynne, J. H., Fulmer, P. A., McCluskey, D. M., MacKey, N. M. and Buchanan, J. P. 2011. Synthesis and development of a multifunctional self-decontaminating polyurethane coating. *ACS Applied Materials and Interfaces*, 3, 2005–2011.

Yu, Y.-J., Hearon, K., Wilson, T. S. and Maitland, D. J. 2011. The effect of moisture absorption on the physical properties of polyurethane shape memory polymer foams. *Smart Materials and Structures*, 20.

Zheng, Y. Q., Deng, S., Niu, L., Xu, F. J., Chai, M. Y. and Yu, G. 2011. Functionalized cotton via surface-initiated atom transfer radical polymerization for enhanced sorption of Cu(II) and Pb(II). *Journal of Hazardous Materials*, 192, 1401–1408.

Zota, A. R., Aschengrau, A., Rudel, R. A. and Brody, J. G. 2010. Self-reported chemicals exposure, beliefs about disease causation, and risk of breast cancer in the Cape Cod Breast Cancer and Environment Study: a case-control study. *Environmental Health*, 9, 16p.

Zukas, W. X., Wilusz, E. and Karasz, F. E. 2004. Permselectivity measurements of ion beam modified barrier membranes for improved chemical/biological protective clothing. *ANTEC 2004 – Annual Technical Conference Proceedings*, May 16–20 2004, Chicago, IL, USA: Society of Plastics Engineers, 2390–2394.

6
Sensors, actuators and computing systems for smart textiles for protection

G. R. LANGEREIS, S. BOUWSTRA and W. CHEN,
Eindhoven University of Technology, The Netherlands

Abstract: Electronic systems with sensors and actuators are enablers for increasing the protection level of textile appliances. Apparel and many other textiles are close to the human body and are part of numerous professional and home routines and tasks. This means that textiles are positioned in our daily life in locations where they can act extremely well for protective purposes by means of monitoring and being responsive. Intelligence created by electronics starts with sensors and actuators integrated into the textile to make it responsive. In addition, a power system, interconnect and processing logic are needed. Some characteristic problems encountered with sensing human parameters can be solved by smart topologies and sensor arrangements.

Key words: sensor network topology, feedback systems, protective actuators, portable power, neonatal monitoring.

6.1 Introduction

There is a special class of textiles that is made interactive by means of active electronics. The interaction is created by distributed sensor and actuator elements, and the decision intelligence unit is a centralised microcontroller. Such electronic systems with sensors and actuators enable a range of textiles to be designed that can provide an increased level of protection. Many textiles including apparel are close to the human body and form part of many professional and home routines and tasks. This means that textiles can be found in places in our daily lives where they can provide a high degree of protection by monitoring the environment and responding to hazards.

It is this high level of integration in our daily lives that makes electronic sensor-actuator systems in textiles so fundamentally different from normal electronic systems. Therefore, this chapter focuses not only on technology for integration, but also on the concepts of placing awareness systems in our direct surroundings. This will be mainly done in Section 6.2. In the next three sections, an overview of the basic electronic elements is given: sensors,

actuators and powering devices. These elements get a special higher-level meaning and functionality when connected into network topologies as described in Section 6.6. In Section 6.7, the future trends that may be expected for electronic intelligent protective textiles are described. Section 6.8 applies the information to a specific design case: the monitoring of premature babies. Some links to information sources are given in the final sections.

6.2 When textiles meet electronics

Textile materials have an established position in our society in many products. They are the preferred materials for apparel and one of the major options for curtains, carpets and furniture. Electronic equipment also occupies an important position in our society. Electronics becomes indispensible when it is used in information exchange, sound, light and motion. It may sound farfetched to ask for an overlap of these two enabling technologies, especially when we also want to place this in the perspective of the protection of humans. However, the unique position of textile appliances so close to our body enables unobtrusive sensing and multi-modal actuators to our perception. When electronics is cloaked by wearing a textile wrapping, it can come closer to our life than ever before.

6.2.1 The position of textiles in our daily life

Textile products are normally close to the body and therefore optimised for human perception. They are an extension of our body and part of our lifestyle. This has a direct consequence on the impact of making them intelligent and responsive. Especially for safety and protection schemes, unobtrusiveness for optimising user compliance is important because people have a natural aversion against systems affecting their autonomy.

In 1998, Hasbro/Tiger Electronics launched the Furby: an interactive toy-robot that mimics social interaction with children. Furby was designed as a textile 'pet' to benefit optimally from the natural affection we have with small animals and textile materials. To satisfy the aim of creating an electronic tool as a personal friend, providing a textile skin was essential. The textile wrapping of the electromechanical toy invited children to bond with the electronic equipment. By this, children were more likely to perceive motion and sound from Furby as expressions of emotion. Bonding was also established by inviting children to take care and to play with Furby. As a reward, Furby grew emotionally and learned more functions.

When we compare this with the Tamagotchi virtual pet, as launched by the Japanese toy manufacturer Bendai two years earlier, we see how big the impact of the form and material on social bonding can be. The

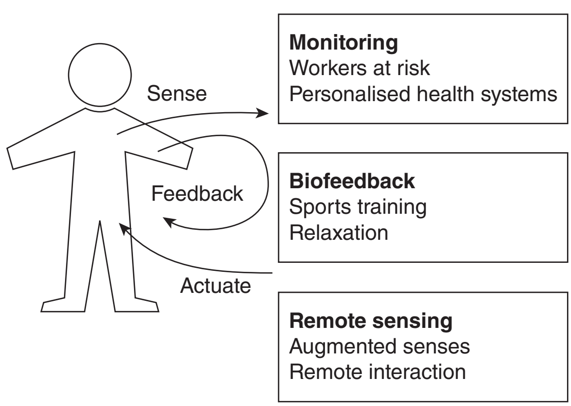
Tamagotchi virtual pet lives in a plastic egg, and is projected onto a display. Just like Furby, it grows as a result of social interaction and care. With Tamagotchi it was almost impossible to mimic emotions, because the pet remained virtual. On the other hand, Furby is immediately seen as a personal friend, which is the result of the shape of a fictitious pet, the motion and sound, but especially the furry appearance.

Although in protection and safety systems, the use of a textile as a substrate is not intended to achieve social bonding up to the same level as Furby, it helps to improve the social acceptance of safety tools. Textile tools for protection and safety systems can solve critical problems when probing and influencing behaviour, depending on the aim of the product. In the following section, protective textile products are categorised according to the direction of data flow.

6.2.2 Data stream categories

By making textiles intelligent and responsive, an information channel is opened between a monitored subject and a monitoring subject. The data stream can be basically in three directions, depending on the application scenario as shown in Fig. 6.1.

First, textiles can monitor a person and send the information to the outside world. This is a scenario applied to working people at risk, to monitor their condition and provide reports to a central control room. It is also an important data direction for personalised healthcare systems, where a patient at risk or under test is being monitored. Our healthcare system has reached a level where the type of conditions we want to observe are occurring infrequently (epileptic seizures, early uterus contractions during pregnancy, heart failures, etc.), or are associated with behavioural and



6.1 Three directions of information flow.

psychological aspects (stress, compulsive disorders, sleep, etc.). Therefore, in this data stream direction, the person being monitored should be unaware of the presence of sensors and electronics, in order to conduct his life or occupation as normally as possible: we do not want to affect the life of the person using or wearing the system.

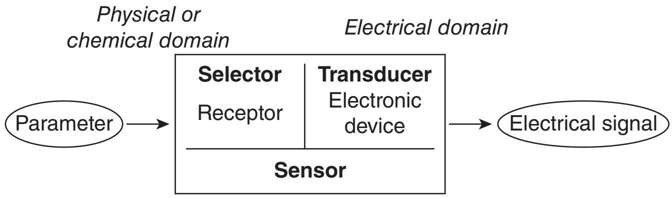
In the second information flow direction, the environment is monitored and the information or response is given to a person by means of intelligent textiles. This direction of data flow opens opportunities for augmented senses: we can make people experience information content that is normally not conceivable with our human senses. In other words: data from a source that cannot be sensed because it is out of our reach (sensory-wise or location-wise) is converted into an information modality that can be sensed. Unlike the previous category, there is not an application example currently available. However, it is used a lot by designers to explore the option of bringing emotions and intimacy from one person to another over larger distances. Many of us are already close to it when carrying our mobile phone in our trouser pocket. By this, we can feel when the phone rings or when a message is received.

The third information stream is where an individual person is monitored, and his own bodily data is offered in another modality to the same human body. Examples of such a short loop data stream is found in (bio)feedback systems. A well established feedback system is on the market by the Polar company (Polar, 2010). Their watches are receiving data from a textile chest belt that measures heart rate. This enables professional and leisure sportsmen to improve their training program. Heart rate is not easily sensed by our human senses. With such a feedback concept we can improve and perform better.

Note that not all product scenarios will fit into the categories represented by the three data flow directions, simply because in some cases, the electronic system does not carry meaningful information. Examples are electronic clothes or stockings for heating the human body and textiles with built-in light for curing light-affected diseases or for wound healing.

6.3 Sensors in textiles

For protecting objects in situations where we cannot judge the situation ourselves, our protection system must start with the collection of data. This is done with sensors. In the scope of this book, we are interested in sensors that can be integrated with textiles; however, the basic phenomena and design problems of sensors apply. This section is not written as an exhaustive list of sensors, but pinpoints the most important sensors used in combination with textiles, based on their operation and application.



6.2 Basic structure of a sensor.

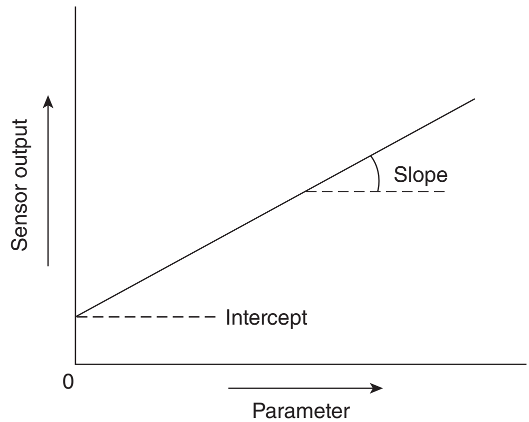
6.3.1 Generic sensor concepts

A sensor is a device that converts information from a domain of interest into a useful electronic signal. In general, this conversion takes place in two parts: a selector and a transducer as indicated in Fig. 6.2. In the selector, the information of interest is converted into a form that is measurable by the transducer. As the transducer part is non-selective, the selector must introduce the desired selectivity (Middelhoek and Audet, 1989).

For many chemical sensors, this two-level interpretation is quite clear. Commonly observed chemical selectors are selective membranes and modified surfaces. Examples of chemical transducers are sensitive transistors or capacitive transducers. Physical sensors normally have a less defined separation between those two parts. For measuring temperature or moisture, selectivity is created by taking a material where one of the material constants changes with temperature or water absorption, respectively. Next, a transducer part is chosen, which converts the modulated material constant into a change of electrical resistance or capacitance.

If a sensor is seen as a transducer of information from one domain to another, two types can be distinguished. The first type is sensors that convert energy from one domain to another. As a result, the output signal will be zero when no input is present because the only energy applied is the energy of the signal itself. This is called a self-generating transducer (Middelhoek and Audet, 1989). Examples are the thermocouple and the dynamo. The second type of transducers comprises devices to which energy is applied by a source, which is subsequently modulated by a physical or chemical parameter. These are modulating transducers (Middelhoek and Audet, 1989): examples are the pH sensing transistor (referred to as ISFET) and the thermistor temperature sensor.

Generally, a sensor should give an output signal as a function of an input signal, related by a certain sensitivity parameter. If a linear relation is assumed, as represented in Fig. 6.3, two things are important: the slope of this relation and the intercept at zero input. The operational model of a sensor device is a mathematical description that links the input uniquely to the output signal. Normally, this requires the characterisation of a slope and a y-axis intercept, either by calibration or complete determination of the



6.3 Linear sensor output.

model. When according to the model a guaranteed zero output is observed at zero input, a one-point calibration will be sufficient; otherwise at least a two-point calibration must be performed.

To come back to the self-generating and modulating sensors, the self-generating transducers have no output signal at zero input. In that case, there will be no offset (intercept in Fig. 6.3) and only the slope has to be known; for example, by a one-point calibration. On the other hand, transducers of the modulating type have a non-zero y-axis intercept, and so the reference is often not well defined.

The dependency on stable references and calibration are the key problems in sensor system applications. With modulating transducers, the offset can sometimes be eliminated by measuring the output with respect to another element that is not sensitive to the measured parameter (Olthuis *et al.*, 2000; 2001). In that case, a zero output means that the conditions at the measuring device are equal to those at the other device. This is a relative measurement with which common undesired signals, such as unstable references, can be eliminated. Relative measurements with respect to a second sensor are referred to as 'differential measurements'. An often-used differential set-up is the Wheatstone Bridge (Cobbold, 1974). The advantage of bridge set-ups is that the output voltage can be set to zero at a desired sensor output by adjusting the trimming element. In addition, interfering signals that are common to the branches are being eliminated intrinsically.

The reason that references and calibration data are not fixed, normally comes from interfering phenomena, such as ageing, temperature, moisture and motion. Especially in textile applications, ageing is strongly present and is accelerated by washing the material. The effect of permanent changes, such as corrosion and the absorption of moisture, is dramatic. The sensors

are said to have a cross sensitivity with another parameter: meaning that they are not only sensitive for the intended parameter, but also for an interfering parameter. In some cases, the cross sensitivity can be eliminated in a differential set-up, but for some parameters this is quite hard in practice.

Motion of the human body has similar spatial and temporal characteristics to the physiological parameters of interest. This means that motion of the human body is distributed over the chest, head and extremities, just like the (electro)physiological data of interest. In addition, motion frequencies ranging from the sub-Hertz to the tens or hundreds of Hertz regime, are in the same frequency band as breathing, heart rate, etc. This means, also, that for signal pre-processing by filtering, we cannot simply suppress a disturbing frequency band. Such interferences of signals due to motion are referred to as 'motion artifacts', and are notoriously hard to eliminate from wearable systems.

In this subsection, we have seen how drift in the offset, slope and reference of a sensor result in the need for smart system solutions. Normally, it is a combination of calibration and differential topologies that is needed to suppress artifacts up to an acceptable level. These topics translate directly into aspects of signal robustness and reliability that will be essential in safety critical systems.

6.3.2 Types of sensors

The separation of sensors into a selector part and a transducer part, as explained with Fig. 6.2 in the previous subsection, makes us aware that several parameters can be measured with different transducer elements. Imagine a selector element consisting of a compressible (textile) material to transform 'touch' or 'pressure' into a material deformation. To convert the deformation information into an electrical signal, several different types of transducers are possible. We could use an electrical resistance measurement (Manunza *et al*., 2006), a piezo-electric measurement (De Rossi *et al*., 2003), an electrical capacitive measurement, or an optical read-out system. When classifying the transducer parts as electrical components, the number of options is limited.

Resistive principles are relatively easy to integrate, because technologies for embroidering, weaving, and knitting conductive wires into textile substrates are available. In addition, resistive elements can be applied to a textile after construction of the textile substrate by lamination. A characteristic property of a resistive element is that the information picked up by it is collected over a larger area. An example is a strain gauge that measures a change in length over the whole size of the element. When applied around the chest, it measures the variation in total circumference, which is a measure

of the breathing rate. This has been known since the early days of textile integration (Mazzoldi *et al.*, 2002).

For textile integrated buttons, the resistive principle has become dominant over earlier capacitive attempts. In the early days, manufacturers of portable devices developed concepts to interact with devices by means of capacitive buttons in textile garments. Examples are from Infineon (Jung and Lauterbach, 2003), Sony (Rekimoto, 2001), and Ericsson (Goldstein and Chincholle, 1999). However, a capacitive method for a textile, in combination with the limited electrical conductance of the textile interconnect, will always result in delays and noise. Delays are the result of the relatively long RC-times, and the noise comes from the high impedance nature of capacitive probes that will act as antennas to pick up electromagnetic signals. Therefore, push buttons in textiles are now generally based on resistive principles. Eleksen is using two layers of conductive textile with a gradient in the applied potential. These two layers form a matrix by which every x and y position can be detected uniquely (Sandbach, 2001, 2002).

The use of resistive transducers is not only limited to mechanical sensors using strain and touch. The selector part can also be a chemically active fibre. An example can be found in a patent of the US Navy (Buckley, 1997), where polyaniline and polypyrrole fibres are used to detect gases such as NH_3, NO_2, and organophosphanates and moisture. Also, examples of hygroscopic fibres that convert moisture into a change of electrical resistance are reported in the literature (Nishijama and Fukui, 1989).

Inductive methods, using magnetic coils, can be more suitable for textile integration than capacitive transducers. Coils can be easily made by embroidery or lamination of metal conductive paths in a textile technology compatible way. Capacitive transducers comprise thin insulating spacers between two conductive layers. In textiles, these spacers are prone to short circuit, destroying the proper operation of the capacitive element. For relatively large surfaces, as available on textiles, embroidered or laminated coils are an option. An example of textile integrated coils can be found from Seoul National University (Roh *et al.*, 2010).

In resistive, capacitive and inductive transducers, the information from and to the sensor head is electrical. A disadvantage of the metal wires needed for electrical systems, is that corrosion may be a problem and the connectors with non-textile modules are a potential risk for errors. An alternative is to use optical fibres, e.g. silicone wave guides. Such fibres can conduct light for information transportation, illumination or signalling. The advantage is that these have a higher chance of being washable than metal wires and are integrated easily into textiles by weaving or other techniques. The transducer part of a sensor can be an optical path. An example is reported by Rothmaier *et al.* (2008) where pressure-sensitive textile prototypes are demonstrated based on flexible optical fibre technology.

For monitoring electrophysiological signals such as electrocardiography (ECG), electroencephalography (EEG) and electromyography (EMG), there is, in fact. no transduction: the signal of interest is already electrical. This means that we can pick up the signal with conductive electrodes on top of the skin. These electrodes can be integrated with a textiles using conductive yarns for wearable applications (Catrysse *et al.*, 2004). In other prototypes, the electrodes are placed in the fixed world, for example a car seat or a bed (Ishijima, 1993). It is not absolutely necessary to have a galvanic contact to the human body: a capacitive coupling may be sufficient because, for electrophysiological signals, we are not interested in the DC value. The principle of using an insulated electrode for capacitive measurements of electrophysiological signals was first demonstrated by Richardson (1967). Only recently has the technology been integrated into textiles (Ouwerkerk *et al.*, 2007; Linz *et al.*, 2007; Gourmelon and Langereis, 2006).

The absence of transduction from one domain to the other does not mean that these signals are easier to work with. Especially with electrophysiological signals, there are interference, motion artefacts, noise, reference problems, etc.

6.3.3 Examples of sensor systems for safety integrated into textiles

For monitoring people at risk, a combination of environmental sensors (temperature, gases, moisture etc.), sensors monitoring the human body (heart-rate, heat flux, etc.) and motion sensors are needed. Such systems can supply this information to the user, or to someone monitoring the user for safety reasons.

An impressive study was done by the Finnish company Reima with the University of Tampere from 1998 until 2000 in the Cyberia project (Reima-Tutta Ltd, 2010; Rantanen *et al.*, 2002). In this project, the aim was to develop an outdoor suit that increases the wearer's possibility to survive in the Arctic regions. The project addressed all technical aspects involved, from user interfaces to high-tech textiles and power management. All the design optimisations were aimed at an increased safety level. One aspect of safety is the identification of an accident. The smart clothing had enough sensors to estimate whether the wearer has a health risk. This was based on temperature, moisture, heart rate and body position. Especially the concept of measuring the environment is essential in making a proper decision about an accident; for example, falling through the ice, in which case the person is wet and cold.

Another example of a safety monitoring system integrated into a textile, was developed in the EU project 'ProeTEX' (Curone *et al.*, 2010). For monitoring firefighters during their work, a set of garments was developed.

The monitored parameters are heart rate, breathing rate, body temperature, blood oxygen saturation, environmental temperature, concentration of toxic gases, such as carbon monoxide and carbon dioxide, operator's activity, and his absolute position and speed.

System solutions for monitoring motion and position are normally based on MEMS (silicon micro-machined) accelerometers and sometimes gyroscopes. These elements are not integrated into textiles but are placed as small boxes on a wearable application (Zephyr, 2010; XSens, 2010). This still means that the mounting needs optimisation for comfort, robustness and proper functioning, where again textiles can bring the ultimate solution.

Physiological measurements of the human body include heart rate, respiration, temperature, etc. Therefore, the sensors are normally close to the skin. Textile electrodes for ECG or heart rate sensing are demonstrated by Textronics, Fraunhofer IZM, and are widely available on the market from Polar. This technology has resulted in some wearable body monitoring systems. For example, SmartLife Technology (SmartLife, 2010) can provide monitoring for detecting fatigue, dehydration or exhaustion. The shirt is a single garment, created with integrally knitted ECG electrodes, respiratory sensors and conductive pathways for interconnection.

Still one of the classic examples of personalised health shirts is the LifeShirt of Vivometrics (2010). It measures respiration based on inductive plethysmography, where a sensor band measures the body cross-sectional area by determining the self-inductance of a flexible conductor encircling the body. The sensor band contains copper wiring integrated into a stretchable band in such a way that the band can still be stretched. The heart rate is measured by means of ECG, and a three-axis accelerometer records patient posture and activity level. Optional peripheral devices measure blood pressure, blood oxygen saturation, tidal CO_2 and other physiologic parameters. All data are transported to a hand-held device, and optionally to healthcare specialists. The LifeShirt is on the market as a medical device that monitors such things as breathing patterns, cardiopulmonary information, and other medical data on ambulatory patients via a wireless connection.

One of the earliest life-monitoring demonstrators was the Mamagoose by Verhaert (2010), developed together with the University of Brussels. It measures respiration by two capacitive elongation sensors, and heart rate by three skin-contact electrodes. It is connected via a wire to a monitoring device that can give an alarm if an unusual situation occurs. In this way it should be able to prevent Sudden Infant Death Syndrome (SIDS). It would be disastrous if such a device gave a false negative or a false positive because the parents would be very distressed. Reliability is therefore crucial with concepts such as Mamagoose. An alternative is Luvion's BabySense

(Luvion Babysense, 2010). This uses sensor pads in the baby bed. When no motion is detected for 20 seconds, or when the respiration rate drops below ten breaths per minute, an alarm goes off.

The development of smart clothing for monitoring people at risk was initiated about ten years ago, and the term 'e-Health' was proposed by Lymberis and Olsson (2003). As they phrase it: 'Both the textile sector and healthcare sector are looking with great interest at the innovative products and applications that could result from the integration of microsystems, nanotechnologies, biomedical sensors, textiles, and mobile telecommunications' (Lymberis and Olsson, 2003). The next logical step is to derive emotional and psychological estimates from the physiological measurements. Situations with psychological stress could be distinguished by EMG measurements (Taelman *et al.*, 2006). Stress estimation, based on heart rate variability, is already common practice, and many more phenomena are derived from it (Waytz, 2010). Heart rate variability has resulted in research into broader platforms with which improved emotional condition estimation can be made (Westerink *et al.*, 2009).

6.4 Actuators in textiles

What actuators can do for us was shown by Berkeley Bionics with their eLEGS in 2010 (Berkeley Bionics, 2010). Their exoskeleton enables paraplegics to walk. Although this technology is not yet integrated into textiles, it is already close to the human body.

This section is about technology to make textiles responsive by means of actuators. Actuators integrated in textiles can be used for two purposes – signalling (haptic feedback, light, sound, etc.) or environment control (heating, illumination). The first category contains information and the second one transfers energy. For protection systems we will see both: signalling to warn a person and energy transfer to create a healthier atmosphere. The latter is the most established: the electric blanket or electric mattress pad which protects us from getting cold.

6.4.1 Generic actuator concepts

With actuator concepts found in the literature, the operational principles are as numerous as the applications. Roughly speaking, for textile applications we see light, sound, heating and motion as the main modalities of actuation. Motion actuation can be based on electrostatic attraction, (electro)magnetic effects, thermal actuation, electrochemical principles, or piezoelectricity, but given the texture and size of textiles, electromagnetic effects (motors) and thermal effects (shape memory alloys) are the most

common. This has to do with the relation between typical size and required forces needed to move things. Due to scaling of the laws of physics in the regime of centimetres and larger, the forces generated by magnetic fields are more efficient than those in electrostatic fields (Langereis, 2006). A shape memory alloy is an alloy that 'remembers' its original shape and can return to the pre-deformed shape by heating. These materials are light-weight, solid-state alternatives to conventional actuators, such as hydraulic, pneumatic, and motor-based systems. The shape options and the small size of the driving units make them very attractive for textile integration. For signalling by means of vibration, where high frequencies are needed, a DC motor with an eccentric mass is the most used actuator.

6.4.2 Examples of protective actuators integrated into textiles

Heaters can be integrated into textiles to prevent hypothermia. A product line is already on the market by Thermologic using T-Ink conductive ink to create the resistive heater elements (Thermologic, 2010). The product line offers gloves and jackets. Also, the Cyberia project (Reima-Tutta Ltd, 2010; Rantanen *et al.*, 2002) included heating as a safety element. When the wearer has dramatic hypothermia, all the remaining power of the system is used for heating after an emergency call is sent.

Putting LEDs into wearables is a success story for artists, as shown by Janet Hansen's Enlighted Designs (Hansen, 2010) and by the more module-based Uranium Jeans products (Uranium Jeans, 2010). A higher integration level is achieved by the Luminex technology that is based on light emitting fibres and also gives impressive effects (Luminex, 2010). None of these products have been developed as safety products. There is, however, a great opportunity to use illumination on wearable textiles for safety, at night, in traffic. Signage on the floor has been developed by Infineon and is now under development at the German carpet manufacturer Vorwerk Teppich (2010). In their business considerations, they do mention the opportunity of floor signage for safety systems.

Haptic actuation is the key technology of Squease™, a vest for young people with Autistic Spectrum Disorder (ASD) (Squease, 2010). Individuals with ASD often have difficulties with processing sensory information, adapting to changes, being in busy environments and interacting with other people. These types of daily experiences can make being in school or on-the-move very stressful. The aim of the garment (Fig. 6.4) is to reduce anxiety in these situations through the application of deep pressure on the upper body. Squease comprises a fashionable hooded sweatshirt and a deep pressure vest, which the wearer can inflate by means of a hand-held controller. Squease enables wearers to apply and control the amount of deep

6.4 Squease^{TM} vest for teenagers with ASD (Squease, 2010). With permission from Squease Ltd.

pressure themselves. The hood of the sweatshirt is lined with a special material, which reduces sounds that people with ASD find unpleasant. Squease is a well developed example of a protective textile product for teenagers.

6.5 Power

A direct consequence of introducing electronic parts into textiles is the need for electric power. Electric power normally needs two forms: supply and storage. First, the energy should be brought to the textile product. This can be done by either generating it in the textile itself (scavenging) or by charging battery elements. Next, storage is needed, because even with scavenging, we can not generate the amount of electrical energy that may be needed at any instantaneous moment.

6.5.1 Batteries

When using non-rechargeable batteries, the supply and storage modality is the same, and is the battery element itself. However, in textile applications this is not the preferred solution because a battery compartment is a potential problem during washing, and the size and mass distribution will negate the intrinsic advantages of using a textile. This means that rechargeable and free-form batteries are preferred for textile applications.

Solicore's Flexion line of lithium polymer batteries (Solicore, 2010) are optimally suitable for textile integration. They are claimed to be flexible, which is not the case with the product line of Free Form Battery (Free Form Battery, 2010) – elements that are rigid after they have obtained their special forms during fabrication.

Integrated charging systems are reported in the literature. Chen *et al.* (2009a) have demonstrated a wire-less power supply based on the principle of inductive contactless energy transfer for use in neonatal intensive care units. The prototype transfers approximately 840 mW of power, and is implemented as a plush animal.

A robust inductive link, with charging of the battery while simultaneous bidirectional data communication is implemented, has been demonstrated by Carta *et al.* (2009). The inductive elements are optimised for textile integration on a flex-and-stretch print. The power link can provide power up to a maximum distance of 10 cm and up to a maximum power of 200 mW. Bidirectional data transfer at a fixed rate of 4.8 kbps is guaranteed during the battery recharge (Carta *et al.*, 2009).

6.5.2 Energy scavenging

'Energy scavenging' or 'energy harvesting' is a method to derive power from available sources. Scavenging can be done from kinetic energy, (sun) light, temperature differences, wind, etc. The challenge is to harvest enough energy to power the application. Fortunately, there is a trend for electronic solutions to use less power, and scavenging techniques are becoming more mature, with the ability to generate higher levels of power. The result is that first working prototypes of scavenging systems are being presented at conferences. For proper scavenging, the amount of harvested energy is proportional to the surface size or volume of the harvesting element. For solar energy, sufficient area to capture light is needed. For thermal energy scavenging, a sufficient temperature difference and a sufficiently large surface are needed. In textiles, there is the unique opportunity to have a large surface area, compared with hand-held or other stand-alone devices. In addition, for wearable textiles, there is also a temperature difference, induced by the heat dissipated from the human body.

The company Konarka Power Plastic (Konarka, 2010) has a photovoltaic material that can be printed or coated inexpensively onto flexible substrates such as textiles, using roll-to-roll manufacturing. With this technology, solar cells can be made on every flexible surface. The material, called 'Power Plastics', can be made in any colour and pattern. Konarka's website shows consumer products (e.g. bags), but also textile tents as electricity-generating buildings for military applications can be made. Any pattern can be applied onto the cover layer.

The University of Southampton recently announced plans (Beeby, 2010) to develop fabrics for clothing that will generate electricity through the wearer's movement and body heat. The smart fabrics will be made by using a rapid printing process to attach a film of piezoelectric or thermoelectric

material to a textile base, which will then be able to harvest energy as electrical power.

6.6 Networks

The previous sections focused on single sensors and actuators. When we combine several sensors, with or without several actuators, there is an advantage. More sensors can help to make the system more robust, or more sensors can be used to get more information about the subject of interest (Langereis, *et al*., 1999).

Some data on the human body are not localised. For example, electrophysiological data (e.g. Electromyography, EMG) is distributed over all extremities and muscles. Also motional information is distributed – in some applications we want to know the relative motion of the arms with respect to the body. In such cases we will need multiple sensors over the body. Examples of situations where the body is seen as a segmented system are wearable systems for fall prevention and systems monitoring risk at athletic sports. The conceptual background of the electrical and informational consequences of distributed sensor/actuator networks is already known from existing large systems with many information sources. We can re-use that knowledge to optimise textile distributed systems for safety and protection.

6.6.1 Generic sensor/actuator network concepts

When combining sensors and actuators in systems, the most common principle used is feedback. In a feedback loop, the result of an actuator is measured and the sensor reading is used to evaluate the effect of the actuator. Based on the outcome, the actuator operation is adjusted. The most common example is the thermostat controlling the temperature in our houses. Based on the desired temperature setting and the measured temperature, the heating system is switched on or off. This results in a room temperature with an accuracy close to the accuracy of the temperature sensor, which would not be an option with a feed-forward system without a sensor. In fact every system that needs to be safe and stable consists of feedback loops. The physiology in our body, like our oxygen control, our temperature, our blood pH, everything is controlled by feedback. It is therefore a good design choice to utilise feedback loops in the sensor–actuator systems for protection and safety. The measurement of core body temperature by means of heat flux is an example of a feedback method (Fox and Solman, 1971).

The feedback loop may include the user, in which case we speak of biofeedback. An example of biofeedback is found in systems for psychological stress estimation and control for relaxation (Feijs *et al.*, 2010).

With sensor arrays, we can do differential measurements as mentioned earlier. The advantage of a differential measurement is that common influences are invisible: the output is determined only by differences between sensors. We can have two types of differential measurement: one where two sensors are measuring at the same time but at different locations, and the other where one sensor is measuring on two different occasions in the same location. In a 'stimulus–response measurement' (Olthuis *et al.*, 2000; 2001; Langereis *et al.*, 2000), a sensor reading is compared with a reading of the same sensor, but after an actuator has changed one single condition in the neighbourhood of the sensor. In that case, all other factors are common to the two measurements, and will cancel out. The cancellation works only if the disturbing factors do not change between measurements, meaning that they have time constants larger than the interval between the two measurements. Sometimes, we can learn new parameters by monitoring the dynamic time response on the applied disturbance.

The most straightforward advantage of multiple sensors with respect to safety-critical systems is the redundancy. By having more statistics about a subject, the extra information results in information about the validity, or can be used to detect whether one of the sensors has become unstable. However, there is a deeper advantage of multiple sensors that may lead to the estimation of new parameters. This is studied in the field of multivariate analysis and explained in the next subsection.

6.6.2 Multivariate analysis

While the aspects of the previous section are mainly on the sensor-head level, we also have a signal processing or mathematical layer where we can apply some multi-modal sensor concepts. Dittmar demonstrated the power of multivariate analysis with a shooting experiment using 'polygraphy', where many physiological body parameters are measured (Dittmar *et al.*, 1995). Based on the combination of responses of physiological parameters, it was possible to distinguish between a successful and an unsuccessful shot. So, a parameter such as 'hit' or 'miss', which cannot be measured with any single sensor on the human body, can be estimated using multivariate analysis.

To make decisions based on many parameters, the mathematical toolbox is obtained from a technique called 'surface response methodology' (Myers and Montgomery, 2009). With this technique, a set of strategically chosen measurements is used to explore the multi parameter space. The optimum location is subsequently chosen from the estimated model of the parameter space. This technique has been successfully applied to find new parameters in complex multi-sensor systems (Olthuis *et al.*, 2000).

Fuzzy logic was developed by Lofti Zadeh in 1965, and has evolved as an alternative to the binary logic of the classical propositional logic. Fuzzy

logic uses soft decisions, which means that, together with the parameter of interest, the validity of the parameter is reported (Zadeh, 1996). In situations where we have a mix of decisions with different levels of importance, fuzzy logic can be interesting.

6.6.3 Network topologies

Besides the interaction model between sensors and actuators, the topological mapping of the network should be considered. A snowboard jacket called 'The Hub' by O'Neill in the winter of 2004/2005 was mainly a design exercise to deal with network issues in electronic textiles. The jacket had partially integrated buttons and wires for an MP3 player, but made use of a Bluetooth connection for communicating with a mobile phone. The Nike ACG CommJacket of 2004 had a similar approach. The Levi Strauss RedWire DLX Jeans, which are iPOD compatible, are still on the market, just like the Scottevest Revolution jacket (Scottevest, 2010). However, although these multi-device apparels are all conceptually strong for carrying entertainment products, it will be a big challenge to find the right network topology for textile safety and protective systems.

6.7 Future trends

The next steps in the development of textile integration should come from two sides: the technology push and the concept development for finding the big market killer applications. Electronic technology is, in principle, low-power and small enough to fit into textiles. However, because the textile designers and electronic equipment manufacturers have only recently found each other, some major steps have to be taken to make both worlds compatible. The following technological developments will result in dramatic changes in what textiles will mean for our environment, including safety and protection.

6.7.1 Trends at the material and device level

Micromachining in silicon, also known as Micro Electro Mechanical Systems (MEMS), was introduced in the 1980s and has enabled many electromechanical and electrochemical methods in the material with which we can already make electronics. The result is that devices such as microphones, accelerometers, biochemical reaction chambers, fluid pumps and fluid mixers have become extremely small, cheap and fast. This has had its impact on society, where sensor and analysis systems are now everywhere (Langereis, 2006). It is a matter of time and awareness before MEMS devices dedicated to protection systems will be optimised for textiles. In principle,

all of our body information is available in the gases, fluids and electromagnetic waves on the surface of our body. MEMS technology can analyse this body information and use it to assist in making decisions to lower the risk of becoming ill or injured. With nanomaterials the level of integration can be a step further and more sophisticated. So the trend of integration and miniaturization does not stop at the micron level. In the future the integration level will be higher and higher until we completely regain the same levels of washability and comfort as are found in non-electronic textiles.

6.7.2 Trends at the system topology level

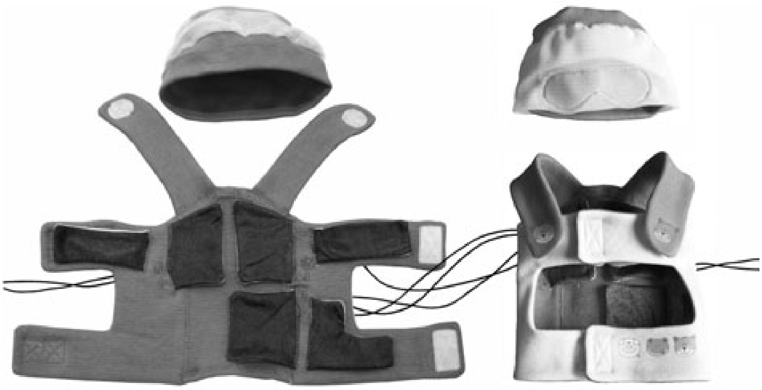
The shift towards wireless technologies makes it possible to connect easily to other objects. This cloud concept will transfer information from human to human, but also from any human to any physical object. The 'Internet of Things' is coming (Kranenburg, 2007), and the impact of having all Internet data available at any low-profile node will change our life. What once started with tags on anything will expand to a world where the position and state of any object is known. It will not only be known for a scanner close to the object, but also to any other object wherever in the world. Data is not anymore stored at localised computers but data will be decentralised and distributed.

Just as we could estimate new immeasurable parameters from polygraphic multi-sensor networks, the global internet of objects and data will give opportunities we cannot yet even imagine. Especially for protection and safety, this must make a big difference. Until now, epidemiological data on diseases could be evaluated only on demand, after people got ill and after the disease was identified. With a cloud of objects and information about many people, we can not only identify diseases at an earlier stage, but also immediately correlate the patterns with all other events in our society.

The current trend towards monitoring mental conditions will expand in future to concepts where mental conditions of multiple people can be mapped. This will be used for risk analysis because stress correlates immediately to accidents, and so, accident prediction becomes feasible.

6.8 Design case study: neonatal monitoring

The Smart Jacket project, with the cooperation of Eindhoven University of Technology (TU/e) and the Máxima Medical Centre (MMC) in the Netherlands, is about relieving the stress of prematurely born babies admitted to the Neonatal Intensive Care Unit (NICU). The monitoring of vital signs, crucial for early intervention and diagnostics, is currently realised by adhesive sensors on the fragile baby skin which causes the baby pain.



6.5 Neonatal smart jacket embedded with smart textiles

Furthermore, the sight of the baby covered in technology hampers parent–child bonding. In this case, textile integration is essential for guaranteeing unobtrusiveness. With the goal of creating a more comfortable and attractive monitoring system, the Smart Jacket design (Fig. 6.5) is under development by TU/e and MMC. The jacket is specifically designed for premature babies in the incubator and during Kangaroo care (which involves the parent holding the baby skin-to-skin on the chest). So far, it contains silver textile electrodes integrated to provide ECG monitoring (Bouwstra *et al.*, 2009). Sensor design and integration for monitoring temperature (Chen *et al.*, 2010a), blood oxygen saturation (Chen *et al.*, 2010b) and respiration have been developed in parallel, as well as a power supply (Chen *et al.*, 2009a) and wireless communication (Chen *et al.*, 2009b), ready to be integrated to form a complete monitoring system.

Since signal robustness and reliability are essential in safely-critical systems, and as the health monitoring of the Smart Jacket suffers from movement artefacts and noise, efforts have been taken to create a 'context aware' ECG monitoring system. As described in Section 6.6 distributed sensing and multi-modal recording are means used to improve reliability. In the context-aware system that is under development for the Smart Jacket, multi-modal data is collected by distributed sensors with the goal of selecting the most optimal ECG signal based on context. The multi-modal data gives information on context and the redundancy offers freedom of choice in which electrodes to select. Data are collected in clinical settings and clues for the basis of a smart algorithm are investigated. Potential clues are, for instance, the relation between the baby's sleeping position (pressure) and textile electrodes which are located both at the front and the back of the jacket. Or, the relation between movements recorded by accelerometers

and artefacts in the ECG. In this way reliability can be improved by selecting the electrodes that are under optimal skin conditions without movement disruption. Safety can also be improved by using contextual information for more accurate alarming; preventing the alarm from going off when it is known to be caused by an external event. If an alarm goes off falsely, medical staff tend to ignore it: this is called the 'crying wolf' effect.

The creation of a reliable monitoring system through signal processing is strongly interwoven with other design aspects; the design process involves a unique integration of knowledge from medical science, industrial design, sensor technology and electrical engineering. The iterative process began with an information search that included user research involving doctors and nurses at the NICU of MMC, and gathering information on users, clinical work domain analysis, technical feasibility and the design opportunities. Requirements were then derived from the information search, forming a base for brainstorming sessions that resulted in ideas about technological challenges, functionality issues within NICU, and aesthetics. Design choices were based on proof of technology and user feedback. The result of this multidisciplinary process was that the design covers various aspects from being an easily extendable platform for technology, which at the same time has a stress-less dressing process and includes precautions for treatments such as phototherapy by maximal skin exposure to light. This design example shows the multidisciplinary challenge of creating safety systems in textiles.

6.9 Sources of further information and advice

It will be clear that there is a good match between protective textiles and electronic textiles. It will also be clear that interactive textile development is not a purely technical challenge. Multidisciplinary teams of designers must develop the system concepts with scientific proof, with user-focused exploration, and using the latest engineered technology.

The technology projects associated with interactive textiles and funded by the European Commission are represented in the Smart Fabrics, Interactive Textile (SFIT) cluster (SFIT cluster website, 2010). In the USA, it is traditionally the Defense Advanced Research Projects Agency (DARPA) responsible for the textile and safety projects concerning soldier's and pilot's clothing, tents and seats (DARPA, 2007).

Conceptual design work on the impact of textiles on our daily life is done by a select number of interactive arts groups. Examples are the whisper[s] group of Thecla Schiphorst at the Simon Fraser University in Vancouver, Canada (Schiphorst, 2010), and Joanna Berzowska's XS Labs (XS Labs, 2010).

6.10 References

Beeby S (2010). Press Release University of Southampton, September 1, 2010. Available from: http://www.southampton.ac.uk/mediacentre/news/2010/sep/10_90.shtml (Accessed 28 November 2010).

Berkeley Bionics (2010). Available from: http://berkeleybionics.com/ (Accessed 28 November 2010).

Bouwstra S, Chen W, Feijs L, Bambang Oetomo S (2009). 'Smart jacket design for neonatal monitoring with wearable sensors', *Proceedings of Body Sensor Networks (BSN)*, Berkeley, USA, pp. 162–167.

Buckley L J (1997), *Conductive Polymer Coated for Chemical Sensing*, US5674752.

Carta R, Jourand P, Hermans B, Brosteaux D, Vervust T, Bossuyt F *et al*. (2009). 'Design and implementation of advanced systems in a flexible stretchable technology for biomedical applications'. *Sensors and Actuators A: Physical*, 156, 1, 77–87.

Catrysse M, Puers R, Hertleer C, Van Langenhove L, Van Egmond H, Matthys D (2004). 'Towards the integration of textile sensors in a wireless monitoring suit', *Sensors and Actuators A* 114, 302–311.

Chen W, Sonntag C L W, Boesten F, Bambang Oetomo S, Feijs L M G (2009a). 'A design of power supply for neonatal monitoring with wearable sensors, *Journal of Ambient Intelligence and Smart Environments*, 1, 185–196.

Chen W, Tung Nguyen S, Coops R, Bambang Oetomo S, Feijs L (2009b). 'Wireless transmission design for health monitoring at neonatal intensive care units', *IEEE the 2nd International Symposium on Applied Sciences in Biomedical and Communication Technologies (ISABEL 2009)*, ISBN 978-80-227-3216-1, Bratislava, Slovakia, November.

Chen W, Dols S, Bambang Oetomo S, Feijs L (2010a). 'Monitoring body temperature of newborn infants at neonatal intensive care units using wearable sensors', *The Fifth International Conference on Body Area Networks (BodyNets 2010)*. Corfu Island, Greece.

Chen W, Ayoola I, Bambang Oetomo S, Feijs L (2010b), 'Non-invasive blood oxygen saturation monitoring for neonates using reflectance pulse oximeter', *Design, Automation and Test in Europe – Conference and Exhibition 2010*, Dresden, Germany, March.

Cobbold R S C (1974). *Transducers for Biomedical Measurements: Principles and Applications*, John Wiley & Sons, New York.

Curone D, Lindo Secco E, Tognetti A, Loriga G, Dudnik G, Risatti M, Whyte R, Bonfiglio A, and Magenes G (2010). 'Smart garments for emergency operators: the ProeTEX project', *IEEE Transactions on Information Technology in Biomedicine*, 14, 3, May 2010.

DARPA (2007), Press release 12 June 2007. Available from: http://www.medgadget.com/archives/2007/06/darpas_stick_on_body_sensors.html (Accessed 28 November 2010).

De Rossi D, Carpi F, Lorussi F, Mazzoldi A, Paradiso R, Scilingo E P, Tognetti A (2003). 'Electroactive fabrics and wearable biomonitoring device', *Autex Research Journal*, 3, 4, December 2003, 180–185.

Dittmar A *et al.* (1995). 'A multi-sensor system for the non invasive measurement of the activity of the autonomic nervous system', *Sensors and Actuators B* 26–27.

Feijs L, Van Boxtel G, Langereis G R (2010). 'Designing for the movements of heart rate and breath', *DeSForM 2010, 6th International Workshop on Design & Semantics of Form & Movement: Design Semantics in Context*, Lucerne, Switzerland, 3–5 November 2010.

Fox R H, Solman A J (1971). 'A new technique for monitoring the deep body temperature in man from the intact skin surface', *Journal of Physiology (London)*, 212, 8–10.

Free Form Battery (2010). Available from: http://www.freeformbattery.com/ (Accessed 28 November 2010).

Goldstein M, Chincholle D (1999). 'The finger-joint gesture wearable keypad', *INTERACT'99, 2nd Workshop on Human-Computer Interaction with Mobile Devices*, Edinburgh, Scotland, 31st August.

Gourmelon L, Langereis G R (2006). 'Contactless sensors for surface electromyography', *IEEE-EMBC '06, 28th Annual International Conference IEEE Engineering in Medicine and Biology Society (EMBS)*, New York, August 30–September 3.

Hansen J (2010). *Enlighted Designs*. Available from: http://enlighted.com/ (Accessed 28 November 2010).

Ishijima M (1993). 'Monitoring of electrocardiograms in bed without utilizing body surface electrodes', *IEEE Transactions on Biomedical Engineering*, 40, 6, June.

Jung S, Lauterbach C (Infineon), 2003. *Keypad Integrated into Textile Items Comprising a Capacitive Readout Circuit*, WO/2003/052541.

Konarka Power Plastic (2010). Available from: http://www.konarka.com (Accessed 28 November 2010).

Kranenburg R (2007). 'The Internet of Things. A critique of ambient technology and the all-seeing network of RFID', *Network Notebooks 02*, Institute of Network Cultures, Amsterdam, 2007. ISBN: 978-90-78146-06-3.

Langereis G R, Olthuis W, Bergveld P (1999). 'Using a single structure for three sensor operations and two actuator operations', *Sensors and Actuators B*, 53(3), 197–203.

Langereis G R, Olthuis W, Bergveld P (2000). 'A demonstration of acquiring specific concentration data by variations in the operating conditions of a non-specific sensor', *Chemometrics and Intelligent Laboratory Systems*, 50, 211–223.

Langereis G R (2006). 'Microsystem technology based sensors for Ambient Intelligence', in Mukherjee S, Aarts R M, Roovers R, Widdershoven F, Ouwerkerk M (eds), *Microsystem Technology for Ambient Intelligence*, Springer, 151–177.

Linz T, Gourmelon L, Langereis G R (2007). 'Contactless EMG sensors embroidered onto textile', *4th International Workshop on Wearable and Implantable Body Sensor Networks*, Aachen, Germany, 26–28 March 2007.

Luminex (2010). Available from: http://www.luminex.it/ (Accessed 28 November 2010).

Luvion Babysense product (2010). Available from: http://www.luvion.nl/babysense/ (Accessed 28 November 2010).

Lymberis A, Olsson S (2003). 'Review: intelligent biomedical clothing for personal health and disease management: state of the art and future vision', *Telemedicine Journal and e-Health*, 9, 4.

Manunza I, Sulis A, Bonfiglio A (2006). 'Pressure sensing by flexible, organic, field effect transistors', *Applied Physics Letters*, 89, 14, 143502:1–3.

Mazzoldi A, De Rossi D, Lorussi F, Scilingo E, Paradiso R (2002). 'Smart textiles for wearable motion capture systems', *AUTEX Research Journal*, 2, 4, 199.

Middelhoek S, Audet S (1989). *Silicon Sensors, Microelectronics and Signal Processing*, Academic Press Limited, London.

Myers R H, Montgomery D C (2009). *Response Surface Methodology* (3rd ed.), New York: Wiley, ISBN 0470174463.

Nishijama J I, Fukui M (1989). *Moisture and Dew-detection Sensor*, EP329436A2.

Olthuis W, Böhm S, Langereis G R, Bergveld P (2000). 'Selection in system and sensor', in: Mulchandani A and Sadik O A (eds), *Chemical and Biological Sensors For Environmental Monitoring*, Washington D.C., Oxford University Press, 60–85.

Olthuis W, Langereis G R, Bergveld P (2001). 'The merits of differential measuring in time and space', *Biocybernetics and Biomedical Engineering*, 21(3), 5–26.

Ouwerkerk M, Pasveer F, Langereis G R (2007). 'Unobtrusive sensing of psychophysiological parameters: some examples of non-invasive sensing technologies', in Westerink J H D M, Ouwerkerk M, Overbeek T J M, Pasveer W F, de Ruyter B, (eds) *Probing Experience: From Assessment of User Emotions and Behaviour to Development of Products*, Philips Research Book Series , Vol. 8, Springer, 163–193.

Polar (2010). Available from: http://www.polar.fi/en/ (Accessed 28 November 2010).

Rantanen J, Impiö J, Karinsalo T, Malmivaara M, Reho A, Tasanen M, Vanhala J (2002). 'Smart clothing prototype for the arctic environment', *Personal and Ubiquitous Computing*, 6, 1, 3–16.

Reima-Tutta Ltd. and Tampere University of Technology, *Cyberia Project – Smart Clothing for an Arctic Environment*, 1998–2000. Available from: http://www.ele.tut.fi/research/personalelectronics/kankaanpaa/projects/Cyberia/index.htm (Accessed 28 November 2010).

Rekimoto J (2001). 'GestureWrist and GEsturePad: unobtrusive wearable interaction devices', *Fifth International Symposium on Wearable Computers (ISWC'01)*, ETH Zurch, 7–9 October.

Richardson P C (1967). 'The insulated electrode: a pasteless electrocardiographic technique', *20th Conference on Engineering in Medicine and Biology*, p 15.7.

Roh J-S, Chi Y-S, Lee J-H, Nam S, Jin Kang T (2010). 'Characterization of embroidered inductors', *Smart Materials and Structures* 19 115020.

Rothmaier M, Phi Luong M, Clemens F (2008). 'Textile pressure sensor made of flexible plastic optical fibers', *Sensors*, 8, 4318–4329.

Sandbach D (Eleksen). *Detector Constructed from Fabric*, US6452479 B1 (2002) and US6333736 B1 (2001).

Schiphorst T (2010). Thecla Schiphorst's Whisper[s] group, http://www.siat.sfu.ca/research/groups/whispers (Accessed 28 November 2010).

Scottevest (2010). Available from: http://www.scottevest.com (Accessed 28 November 2010).

SFIT cluster website (2010), Available from: http://csnej106.csem.ch/sfit/ (Accessed 28 November 2010).

SmartLife (2010). Available from: http://www.smartlifetech.com/ (Accessed 28 November 2010).

Solicore (2010). Available from: http://www.solicore.com/flexion-batteries.asp (Accessed 28 November 2010).

Squease Ltd. (2010). Available from: http://www.squeasewear.com/ and http://www.yankodesign.com/2009/07/09/safe-wrap/ (Accessed 28 November 2010).

Taelman J, Van Huffel S, Adriaensen T, Spaepen A, Langereis G R, Gourmelon L (2006). 'Contactless EMG sensors for monitoring musculoskeletal disorders', *IEEE-EMBS, IEEE Benelux Chapter on Engineering in Medicine and Biology*, 7–8 December, Brussels, Belgium.

Thermologic (2010). Available from: http://www.thermologicgear.com/ (Accessed 28 November 2010).

Uranium Jeans (2010). Avaliable from: http://www.uranium-jeans.com/ (Accessed 28 November 2010).

Verharet, Mamagoose: *Sudden Infant Death Syndrome Monitor*, (2010). Available form: http://www.verhaert.com/cms/images/stories/pdf_in_text/verhaert_mamagoose.pdf (Accessed 28 November 2010).

Vivometrics (2010). Available from: www.vivometrics.com (Accessed 28 November 2010).

Vorwerk Teppich (2010). Available from: http://www.vorwerk-teppich.de/sc/vorwerk/thcarper_orgatech_en.html (Accessed 28 November 2010).

Waytz A (2010), 'Psychology beyond the brain: what scientists are discovering by measuring the beating of the heart', *Scientific American on-line*, October 5. Available from: http://www.scientificamerican.com/article.cfm?id=the-neuroscience-of-heart (Accessed 28 November 2010).

Westerink J H D M, Vries G-J de, Waele S de, Eerenbeemd J van den, Boven M van, Ouwerkerk M (2009). 'Emotion measurement platform for daily life situations'. *International Conference on Affective Computing and Intelligent Interaction*, 1, 704–708.

XSens (2010). Avalable from: http://www.xsens.com/ (Accessed 28 November 2010).

XS Labs (2010). Available from: http://www.xslabs.net/ (Accessed 28 November 2010).

Zadeh L A (1996). *Fuzzy Sets, Fuzzy Logic, Fuzzy Systems: Selected Papers by Lotfi. A. Zadeh*, edited by K G Klir and B Yuan, World Scientific Press, ISBN 9810224214.

Zephyr (2010). Available from: http://www.zephyr-technology.com/ (Accessed 28 November 2010).

7

Biomimetic approaches to the design of smart textiles for protection

V. KAPSALI, Northumbria University, UK (formerly at Middlesex University, UK)

Abstract: Biomimetics is a hybrid discipline that enables the transfer of technology from biological systems into the man-made world. Nature is regarded as a source of inspiration for solutions to problems encountered in various areas of engineering. Biomimetic technologies have already found commercial applications in the textile sector that reduce the environmental costs of production. This chapter discusses relevant aspects of biomimetic design and explores ideas that could enrich the design and development of smart protective textiles.

Key words: smart materials, biomimetic design, protective textiles.

7.1 Introduction: smart material design in nature

Imagine a material or structure that could grow, self-repair, reproduce, sense and respond to its environment by adapting its properties and/or behaviour. From autonomous space suits (Banks, 1993) to *Bio-fabrics* made from genetically modified botanical tissue (Ballard, 2001), science fiction writers describe visions of symbiotic garment systems that extend the natural abilities of the wearer and, to a certain extent, become an additional prosthetic organ. They envisage a huge shift in the functionality of clothing that will ultimately blur the boundaries between wearer and garment. These ideas are no longer simply the realm of science fiction; innovations in material science have permeated sectors such as technical textiles to create new products that challenge our perception of textile functionality (textile scaffolds used for medical implants made from smart polymers and gels; military and surveillance garments with interwoven electronic circuitry to enable remote communication; infant clothing incorporating temperature-sensitive pigments that signal overheating to help prevent cot death). Current technology push is directed towards the synthesis of textiles that behave (to various extents) like living organisms. There are countless examples of adaptive, multifunctional materials and structures in biology that could act as paradigms for the design of smart textiles.

Polymath Otto Schmitt invented a pivotal electronic component known today as the *Schmitt Trigger* as part of his doctoral work in the 1930s. The design of the device was inspired by Schmitt's study of the human nervous

system but, unable to identify an existing phrase to describe the translation of ideas from biology to engineering design, he coined the term *biomimetics*. Other popular synonyms used across the world are bionic, biomimicry and biognosis.

Biomimetics has already delivered several commercial technologies to the technical textile sector that offer alternative and arguably improved functions to existing practice. The *Lotus Effect*, for example, is a nano-scale treatment inspired by the surface geometry of the lotus leaf and attributes superhydrophobic, self-cleaning, stain-resistant properties to the textile to which it is applied. The technology was developed by biologists Barthlott and Neinhuis from the University of Bonn in 1975 (Barthlott and Neinhuis, 1997). It offers a low energy, less polluting method to standard coatings made from silicone or organofluorochemicals (Slater, 2003).

Morphotex™ (Teijin Fibre Corporation) is a fibre that demonstrates structural (instead of pigment) colouration; the technology is based on the design of the brilliant blue South American *Morpho* Butterfly wing. The Morphotex fibre is composed of 61 alternating nylon and polyester layers, to produce a colour range of iridescent blue, green and red without the use of pigments. This technology offers an alternative, less hazardous method for introducing colour to textiles. Unfortunately, Morphotex fibres are not commercially available because low market demand prevents the production of sustainable volumes.

There are significant restrictions on available resources for making things in nature; this means that in order to survive, organisms have had to evolve clever ways of optimising the way they use materials. For the purposes of this argument, if we regard evolution in its broadest sense as a form of 'design development' (stretched out over millions of years with tiny incremental changes), bearing in mind there is no designer but a process of natural selection, good design survives while bad design does not (Vogel, 2003). We have significantly more types of material to make things with; this allows us to think less about the way we engineer mechanisms and structures. There are many lessons we could learn from the limitations and consequent solutions found in biology.

Intrinsic material properties are at the very core of our cultural evolution. We define history by the landmark material technology of the period, e.g. stone, bronze, iron ages. The invention and consequent mass production of synthetic polymers revolutionised fashion in the 1950s. Cheap, super-lightweight stockings (*nylons*) rapidly superseded their exclusive silk counterparts and were available to all. In 1969, as Neil Armstrong took 'one small step for man, one giant leap for mankind' and planted a nylon flag on the surface of the moon in a suit made from 30 layers of nylon and aramid fibres, synthetic materials captured the world's imagination and became the epitome of the *space-age*.

Most engineers, luckily, do not face the same penalties if they get a design wrong; however, our approach to the design and production of new materials is somewhat deterministic. This is inevitable because all designers work to a brief that outlines the product requirements prior to the start of the design process. What is difficult to accommodate with this model is change. What happens when conditions alter and different performance is required, or indeed the item becomes damaged? In the situation where manual adjustments to alter functionality or repair are either impossible (by design) or too 'expensive', the entire product becomes unsuitable and is replaced.

There is a fundamental difference between the nature of materials in biology and those of the man-made world: we design *with* materials while materials *become* in nature. We rely on the material to deliver properties such as strength, toughness etc. When we need a structure to demonstrate property X and we do not have a material that delivers the specific performance, we synthesize one that does. As a result, there are over 300 man-made polymers currently in use. There are two main polymers that form the basis of all biological materials and structures; protein and polysaccharide (Vincent *et al.*, 2006). Variations in the assembly of these materials deliver the vast range of properties demonstrated in biological materials. Insect cuticle, for instance, is made from protein and chitin, yet can demonstrates a host of mechanical properties: it can be stiff or flexible, opaque or translucent, depending on the way the raw materials are put together (Vincent, 1982).

Materials and structures in nature are responsive: they alter and adapt their properties to accommodate changes in requirements. Penguins live in conditions of extreme cold and dive to depths of 50 m underwater to feed. The secret of their survival is in the dual functionality of their coat and its ability to adapt to changes in functional requirements. On land, their coat provides a highly effective insulation barrier; in the water, the coat transforms to a watertight skin that enables the animal to hunt efficiently in the deep sea. The multifunctional/ adaptive nature of such biological mechanisms presents great opportunity for the design of smart materials.

Biological structures are far more complex than those made by man. If we look at the hierarchy of a single organism, there are nine levels of organised structural elements: atom, molecule, macromolecule, sub-cellular organelles, cells, tissues, organ, organ system and organism. The organisation of raw materials within and across each level is what enables the rich diversity in properties demonstrated by biological structures (Tirrell *et al.*, 1994). We tend to use less complex, non-hierarchical design processes.

Lakes (1993) defined Hierarchy Order by the number of levels within a recognised structure. The Eiffel Tower is a third order design while skyscraper buildings adopting conventional engineering design, such as the World Trade Center (New York), are first-order designs. The effect of

differences in structural hierarchy between the two types of building is in the amount of material required to achieve the desired strength and the quality of the raw materials used. Lakes (1993) compared relative density ρ/ρ_o (structural density ρ, mass per unit volume of structure, divided by material density ρ_o, density of material of which it is made) of both buildings and found that the relative density of the Eiffel Tower is 1.2×10^{-3} times that of iron (which is weaker than structural steel) while the World Trade Center was made from structural steel and had a relative density of 5.7×10^{-3}. It is clear that significantly less material was used to construct the higher order structure although the raw material itself had inferior strength. Clever design does not always need to rely on the nature of the raw materials to deliver key properties.

Textiles are multiple hierarchy structures. Key textile properties are introduced to the system through the choice of fibre; for example, tensile strength, conductivity, elasticity, and relationship to moisture. Yarn blend, type and twist can affect aspects such as the texture, strength, and permeability to heat, air and moisture. The construction method (knit, weave, non-woven) influences dimensional stability, durability, permeability, etc. This is a very general description and is by no means exhaustive; however, it indicates that there is opportunity to manage the performance of a textile at every level of the hierarchy. Currently, there is more opportunity at the lower (fibre) stages. The question at hand is: can biology show us how to optimise the performance of textiles through hierarchy design without relying on specific properties of raw materials? Can we design a lightweight ballistic vest from cotton instead of Kevlar?

Biomimetics offers a platform that facilitates the transfer of technology from biology to the man-made world. Initial outcomes, such as the Lotus Effect and Morphotex, deliver useful functionalities that reduce the impact of textile and garment production on the environment, but these represent merely the tip of the iceberg. There is a plethora of paradigms in biology that could present solutions or inspiration for the design of smart textiles; we could also discover ways of improving or optimising existing technology to create textiles that adapt and respond to stimuli without necessarily using materials that are costly to the environment and ultimately the consumer. The next section reviews existing biomimetic developments that focus on smart textiles for protection and discusses relevant biological mechanisms that deal with various aspects of protection.

7.2 Biomimicry of smart protective textiles

The protective textile sector is a dynamic driver in smart textile innovation. Designers call upon 'smart' technologies to engineer solutions they cannot execute efficiently or achieve using conventional technology. Propelled by

increasingly demanding and sometimes contradictory specifications (e.g. tougher, harder, lighter), combined with the permeation of new hybrid technologies, the boundaries of functionality and application have been ruptured. Clothing, for example, that enables remote monitoring of body functions, integrated personal computers, mobile phones, etc. would not be possible without the fusion of electronic and textile technology. Wearable electronics is just one of the emerging technologies driving the future of the protective textile industry.

The requirements are very specific. By definition, smart protective textiles (SPTs) need to sense a predetermined threat and respond by actuating a defence mechanism that protects the individual(s) or object(s) it covers/encloses. In terms of clothing, types of threat can be real or imaginary, psychological or physical (Augé, 1995; Bolton, 2002). This chapter will explore opportunities for SPTs presented in a small selection of biological examples in the context of real, physical threat. The aim is to give a few examples of how technology can be transferred and begin to create an understanding of how methodologies can be shaped.

7.2.1 Camouflage

Certain species of animal have evolved surface markings and colouration that function as a primary form of defence: they can blend in with their environment (crypsis) or mimic the appearance of others (Batesian or Müllerian) and so avoid detection by predators. Camouflage is an important area of protective textiles, used mainly in military and surveillance operations. It can conceal the wearer or large machinery when observed (eye, photography or wider band of electromagnetic spectrum) from a distance, thus preventing attack. The key limitation with this type of technology is that patterning and colour remain unaltered, making the material suitable only for specific environments. Also, when machinery needs to be concealed for long periods of time, the camouflage system will not adapt to seasonal changes in the surrounding environment. There is opportunity for SPT in adaptive camouflage.

Chameleons are iconic creatures, known for their ability to mimic the colours and patterns of their surroundings, but there are many more species that can adapt their appearance. *Miomantis paykullii* live in grassy landscapes that are predominantly brown during periods of prolonged drought but can turn green from rapid plant growth after a sudden storm. The nymph of *M. paykulli* relies on crypsis to avoid detection and has evolved a clever adaptive colouration mechanism that detects changes in environmental relative humidity and turns the nymph green (Edmunds, 1974).

Cephalopods (octopus are part of this group) undoubtedly display the most remarkable adaptive colouration. They draw upon highly sophisticated skin to create complex visual displays used, not only to prevent detection, but to intimidate predators and communicate with other cephalopods. The adaptive colouration mechanism is controlled by a combination of hormones and the animal's nervous system. The skin contains chromatophores: tiny sacks containing pigment, that can expand and contract to reveal or conceal the pigment. These sit on layers of light-reflective tissue (irridophores) made from tiny sheets of reflective plates. The cephalopod is able to alter the colour reflected by the irridophores by changing the distance between the layers of reflective plate. In 2007, a team led by Professor E. Thomas of Massachusetts Institute of Technology (MIT), developed a smart gel based on the cephalopod's skin structure. The team used a self-assembling block copolymer thin film made from layers of polystyrene and poly-2-vinyl-pyridine. The thickness of the layers controls the refractive indices and thus the colour of the reflected light. The poly-2-vinyl-pyridine layer is designed to alter its thickness in response to stimuli such as pH and salt concentration, thus changing the gel's colour (http://web.mit.edu/newsoffice/2007/techtalk52-6.pdf).

7.2.2 Impact resistance

Textiles of this type are designed to shield the wearer from penetration of high-velocity objects such as bullets, knives, shrapnel, etc. Ballistic protection depends on the textile's ability to absorb energy locally and on efficiency/ speed of transferring absorbed energy of impact to the crossover points of yarns (energy from the impacting object is dissipated by stretching and breaking yarns). Silk was originally used in the construction of protective garments but high-modulus, high-strength aromatic polymer fibres such as Kevlar (DuPont) are now used. These polymers are composed of highly aligned, long molecular chains, held together by strong bonds. Kevlar yarns are densely woven into plain or basket weave structures. Plates made from hard materials such as steel and ceramics are used as inserts to reinforce protection of vital areas of the body (Chen and Chaudry, 2005). Protection from high-velocity impact with a bladed object poses an additional set of requirements. Unlike a bullet, the blade of a knife can be very sharp and can slice through a textile. The main materials used in this case to protect wearers are aramid fibres/yarns and chain-mail (Scott, 2005).

The requirements of military or security body armour are very similar to those of the reinforced external coverings of heavily armoued creatures, such as armadillos. Predator attacks usually involve scratching and biting. Therefore, protective structures need to prevent penetration from the aggressor's teeth, beak, nails, claws, etc. Pointy spines are used to form

barriers that physically injure the attacking animal upon initial impact, thus discouraging further efforts, e.g. sea urchin spines. Hedgehogs and echidnas roll up into a ball to protect their head and ventral parts, and erect dorsal and lateral spines. Animals such as armadillos, pangolins, woodlice and millipedes are protected by tough, horny plates that will resist repeated impact.

The Dinosaur eel, *Polyoterus senegalus*, is a fish that retains an incredibly tough yet ancient form of dermal armour (hence its name). Tough, high penetration-resistance skins were common in prehistoric fish because there were many large, invertebrate predators around. There are much fewer around today so this mechanism was gradually phased out as it became less advantageous. *P. senegalus* is a cannibal and is believed to have maintained its dermal structure because its main threat is its own species (Bruet *et al*., 2008). Bruet studied the scales of *P. senegalus* and found that they are composed of four layer of materials with very different mechanical properties. Focusing on indentation modulus E and Hardness H, findings revealed that the outer surface of the scale is approximately 10 μm thick and is composed of guanine, a very hard, enamel-like material (E = ~62 GPa, H = ~4.5 GPa). This is followed by 50 μm of dentine (E = ~29 GPa, H = ~1.2 GPa), 40 μm of isopedine and 300 μm of a bone basal plate (both materials E = ~19 GPa, H = ~0.7 GPa). The findings show that the indentation modulus and hardness decrease as they approach the inner surface of the scale. Each layer also has different deformation and energy dissipation mechanisms. The top stiff guanine layer transfers load to the softer dentine layer, which dissipates energy via plasticity. This is lined by isopedine, whose microstructure cracks during deeper penetration in a way that minimizes impact on the structure.

The scaly-foot snail (*Crysomallon squamiferum*) inhabits one of the most hostile environments on Earth; the deep sea volcanic vents of the Central Indian Ridge. The snails have evolved remarkable exoskeletal structures that enable them to live in such extreme conditions and resist attack from crabs, their main predators. The crabs will squeeze the scaly-foot snail in their claws for days if necessary, but the unique shell structure allows the animal to withstand these kinds of pressures (Yao *et al*., 2010). Yao studied the structure of the shell and found a three-layer system comprising two stiff mineralised layers with a thick organic layer sandwiched between them.

Current military body armour, designed to protect against high velocity bullets, can weigh about 15 kg, while a bomb protection outfit can weigh 30 kg (Scott, 2005). The structural design of *C. squamiferum* and *P. senegalus* could be drawn upon to inspire the creation of lighter weight body armour made from multilayer textiles, using less tough and heavy material to deliver equal if not superior protection, that does not burden the wearer.

7.2.3 Auxetic materials: smart blast protection

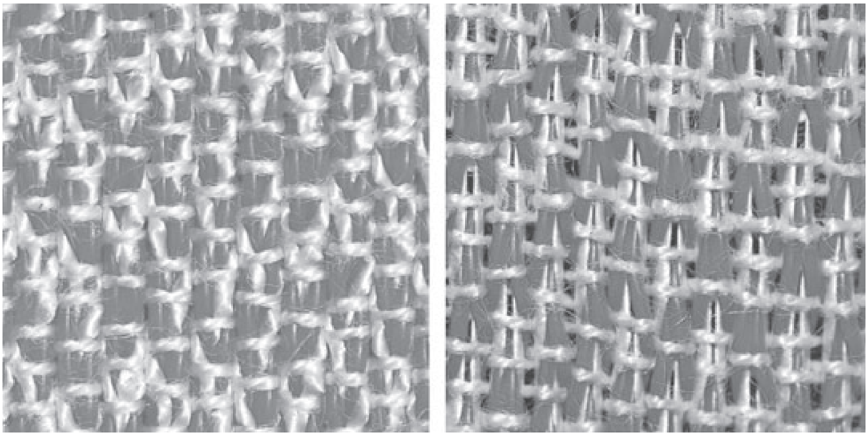
Conventional materials become fatter when compressed and thinner when stretched. The ratio of transverse contraction to longitudinal extension strain in the direction of the stretching force is known as the Poisson ratio (ν). Most engineering materials have a $\nu = 0.3$ (Kevlar 0.35, aluminum 0.32, titanium 0.33): cork has $\nu = 0$. In practice, this means that when you apply pressure to the top of a cork to squeeze it into a bottle top, it demonstrates no dimensional change. When you try to do the same with a stopper made from synthetic rubber, the bottom expands, thus preventing the stopper from sealing the bottle top; you need to twist the rubber stopper in order to get it into place.

Materials with negative Poisson ratio (auxetic) are counterintuitive; they become narrower when compressed and thicker when stretched. By a clever design principle, auxetic structures can be made from simple materials such as paper. As materials approach $\nu = -1$, they become highly compressible but difficult to sheer; they are tougher and more resistant to tearing (Lakes, 1993).

Auxetix Limited is an award winning UK company that owns exclusive rights and IP to a helical-auxetic yarn system. Textiles using this technology (branded *Zetix*) offer enhanced performance in many applications, ranging from aerospace to smart textile sensors. Zetix woven textiles can be engineered to provide blast protection: the structure's ability to deform without failure and dissipate energy over a large area involving many fibres (like a spider's web that remains intact when a flying creature impacts it), enables effective shrapnel capture. The thousands of pores that open up over the surface during impact, 'vent' the blast waves, while the elastic core of the helical-auxetic yarns are resilient – they do not fracture like conventional ballistic resistant textiles (R. Hook, Director of Auxetix Ltd, personal communication, 2011). Figure 7.1 demonstrates the functionality of the fabric under unstretched and stretched conditions. Auxetix Ltd is currently collaborating with the University of Exeter and three other partners on a project funded by the Engineering and Physical Sciences Research Council (EPSRC), applying this technology to the design of a blast-resistant curtain that can capture debris such as glass, protecting individuals working or living in buildings within conflict areas, (http://www.epsrc.ac.uk/newsevents/news/2010/Pages/blastproofcurtain.aspx).

7.2.4 Protection from heat and cold

Predators are one of many threats encountered in the natural world. Sudden changes in environmental conditions (e.g. current global warming) can prove catastrophic. Although organisms can adapt to slow changes, predictions suggest that a 2°C increase of global temperature over the next 90



7.1 Auxtetic textile: (a) unstretched, (b) stretched. Source: Dr P. Hook, Auxtetix Ltd.

years would put 20–30% of species at high risk of extinction (Schneider *et al*., 2007).

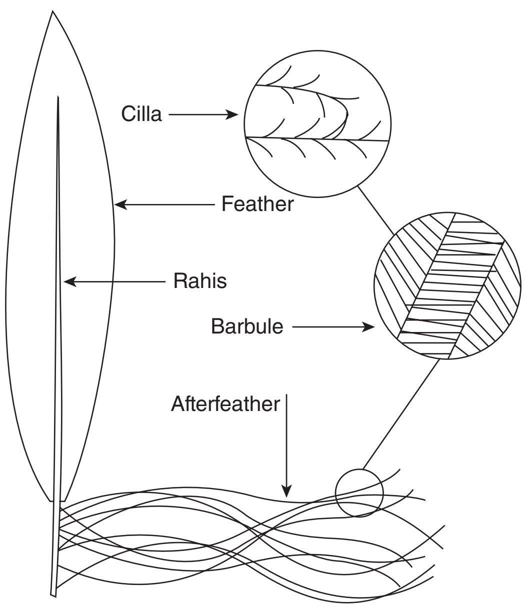
Animals that inhabit extremely cold environments have evolved ingenious coats of fur or feathers that prevent precious body heat from escaping. Grojean (1980) studied the brilliant white coat of the polar bear and found that the pelt itself consists of a dense, insulating layer of fur, about 1 cm long, with fine fibres (25–75 μm diameter) and thick hairs approximately 100–150 μm in diameter and 6–7 cm in length. These are attached to a thin layer of black skin, approximately 1 mm thick. The longer hairs are hollow in structure along their length and taper to a solid edge at their tip. Although they have a smooth external surface, the core is very rough, while the hairs themselves contain no pigmentation. The air pockets created in the hair's core offer additional insulation (Grojean *et al*., 1980). Similar cross-sections are used to create insulating hollow fibres from man-made polymers, introducing additional air pockets into a textile system. The advantage of using man-made fibres, especially in textiles used in clothing or products that will be carried around (i.e. sleeping bags), is that they are lighter than wool or any other insulating natural fibre.

An animal's coat needs to insulate the animal from cold, yet allow heat generated from activity to escape when necessary. There are numerous examples in biology. However, most coated animals do not experience sudden changes in environmental conditions and therefore do not need to alter the functionality of their fur or feathers; we do! Our built environment is laced with interconnected yet individual spaces; each defined by unique thermal and moisture conditions; transition from one to the other can be as instant as walking through a door. Can we design SPT systems that will

sense and react to changes in environmental conditions by adapting the garment properties to manage microclimate conditions in a way that will protect the wearer's thermal regulation?

A remarkable example of adaptive behaviour is in the design of the penguin coat. As mentioned earlier, penguins must withstand extreme cold for up to 120 days without food and then be able to dive up to 50 m into freezing waters in order to feed. When necessary, the penguin coat provides highly efficient insulation that minimises heat loss through radiation and convection, with structural properties that function as an excellent wind barrier, eliminating heat loss though convection. Yet when the animal needs to dive for food, the coat transforms into a smooth and waterproof skin, eliminating any trapped air. This switch in functionality is achieved by a muscle attached to the shaft of the feather; when the muscle is locked down, the coat becomes a water-tight barrier, and when released, the coat transforms itself into a thick, air-filled, windproof layer. The feathers also have numerous large hooks that bind neighbouring feathers into a coherent membrane.

The feathers in a penguin's coat are packed evenly over the animal's body, averaging 30–40 per cm^2. Figure 7.2 illustrates the structure of a typical penguin feather. Dawson *et al.* (1999) and Wan *et al.* (2009) identified that the mechanism responsible for the insulation properties is found in the afterfeather (Fig. 7.2). The diameter of the afterfeather fibres (barbs) is



7.2 Structure of penguin feather. Source: Dawson, 1999.

approximately 5.5 (± 0.9) μm (Wan *et al*. 2009) and consists of approximately 50 barbs averaging 24 mm in length (Dawson *et al*., 1999). Each barb is covered with around 1250 barbules that are about 335 μm in length. This structure creates airspaces of around 50 μm in diameter, which provide an enormous volume for trapped air, thus creating a structure capable of providing such high levels of insulation (Dawson *et al*., 1999). Wan (2009) found that higher resistance to radiative heat transfer is closely related to the fineness of the fibre at the same fibre volume fraction. They compared radiative heat transmission properties of fibres with different diameters: Duck and penguin fibre down exhibit similar diameters 4(± 0.6) μm and 5.5 (± 0.9) μm respectively, polyester 17.6 (± 0.2) μm and wool 26.6 (± 6.1) μm.

A key factor in the success of the adaptive mechanism is the ability to recreate a uniform division of air space every time the coat's functionality switches from waterproof to high insulation. The mechanism that enables this is found on the surface of the barbules – Dawson *et al*. (1999) noticed that tiny hairs known as cilia covered the barbules that function as a stick–slip mechanism to keep the barbules entangled and maintain the movement in directions relative to one another to ensure uniformity in the creation of air pockets during the coat's function change.

So, the insulation properties of the penguin's coat adapt by varying the volume of air trapped within the system by drawing the feather towards the skin when the waterproof functionality is required, and releasing it when the penguin needs to be kept warm. Attempts to interpret this mechanism into garments have led to the creation of an experimental textile system referred to as *Variable Geometry*. The structure is made of two layers of fabric, which are joined together by strips of textile at a right angle to the plane of the two fabrics. By skewing the two parallel layers, the volume of air between them reduces, and this results in a reduction of thermal resistance. The idea has been used in the design of military uniform systems that can be adapted to function in both extreme cold and hot conditions. This was commercialised in 2002 by Gore & Associates, who created an ePTFE membrane and polyester structure (76%PE: 24%PTFE), to be used as a garment insert, under the brand name *Airvantage*. The product allows the user to inflate/deflate the jacket, thus adjusting the garment's insulation properties.

7.3 Conclusion and future trends

The functional profile of textiles in their wider context is changing. Fuelled by innovations in materials science, textile structures are becoming *soft machines*, able to heat, sense, actuate, protect, etc., and eventually become symbiotic structures integrated into many aspects of our lives. Biomimetics is a platform that facilitates transfer of technology from nature to the

man-made world. Initial outcomes have been innovations, such as the Lotus Effect and Morphotex, which offer useful functionalities, able to reduce the impact of textile and garment production on the environment. Biological materials and structures are 'smart' by nature; they need to enable a multitude of mechanisms necessary to support life; they also need to protect, repair, maintain and adapt to changes in the environment. This chapter has begun to illustrate the huge potential for biomimetic design that could inform, even inspire, the development of smart protective textiles.

7.4 Acknowledgements

Special thanks are due to Professor Julian Vincent (University of Bath), Phil Gibson (Natick), Dr Patric Cook (Auxetix Ltd) and the staff at Middlesex University for their advice and support in writing this chapter.

7.5 References

Augé, M. (1995) *Non-places; Introduction to an anthropology of Supermodernity*, London, Verso.

Ballard, J. G. (2001) *Say Goodbye to the Wind. The Complete Stories of J.G. Ballard*, London, HarperCollins Flamingo.

Banks, I. (1993) *Descendant. The State of Art*, London, Orbit.

Barthlott, W. and Neinhuis, C. (1997) Characterisation and distribution of water-repellent, self-cleaning plant surfaces. *Annals of Botany*, 79, 667–677.

Bolton, A. (2002) *The Supermodern Wardrobe*, London, V&A Publications.

Bruet, B. J. F., Song, H., Boyce, M. C. and Ortiz, C. (2008) Materials design principles of ancient fish armour. *Nature Materials*, 748–756.

Chen, X. and Chaudry, I. (2005) Ballistic protection. In Scott, R. A. (ed.) *Textiles for Protection*, Cambridge, UK, Woodhead Publishing.

Dawson, C., Vincent, J. F. V., Jeronimides, G., Rice, G. and Forshaw, P. (1999) Heat transfer through penguin feathers. *Journal of Theoretical Biology*, 199, 291–295.

Edmunds, M. (1974) *Defence in animals*. Prentice Mall, New Jersey, p. 35.

Grojean, R. E., Sousa, J. A. and Henry, M. C. (1980) Utilization of solar radiation by polar animals: an optical model for pelts. *Applied Optics*, 19, 339–346.

Lakes, R. (1993) Materials with structural hierarchy. *Nature*, 361, 511–515.

Schneider, S. H., Semenov, S., Patwardhan, A., Burton, I., Magadza, C. H. D., Oppenheimer, M., Pittock, A. B., Rahman, A., Smith, J. B., Suarez, A. and Yamin, F. (2007) Assessing key vulnerabilities and the risk from climate change. In Parry, M. L., Canziani, O. F., Palutikof, J. P., Linden, P. J. V. D. and Hanson, C. E. (eds.) *Climate Change 2007: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge, UK, Cambridge University Press.

Scott, R. A. (2005) Military protection. In Scott, R. A. (ed.) *Textiles for Protection*, Cambridge, UK, Woodhead Publishing Limited.

Slater, K. (2003) *Environmental impact of textiles*, Cambridge, UK, Woodhead Publishing Limited.

Tirrell, D. A., Aksay, I., Baer, E., Calvert, P. D., Cappello, J., Dimarzio, E. A., Evans, E. A., Fessler, J., Hoffman, H. D., Jaffe, M., Mayer, G., Mow, V. C. and Wainwright, S. A. (1994) *Hierarchical Structures in Biology as a Guide for New Materials Technology*, Washington, D.C., National Academy Press.

Vincent, J. F. V. (1982) *Structural Biomaterials*, Princeton, Princeton University Press.

Vincent, J. F. V., Bogatyreva, O. A., Bogatyrev, N. R., Bowyer, A. and Pahl, A.-K. (2006) Biomimetics: its practice and theory. *Journal of the Royal Society Interface*, 3, 471–482.

Vogel, S. (2003) *Comparative Biomechanics: Life's Physical World*, New Jersey, Princeton University Press.

Wan, X., Fan, J. and Wu, H. (2009) Measurement of thermal radiative properties of penguin down and other fibrous materials using FTIR. *Polymer Testing*, 28, 673–679.

Yao, H., Dao, M., Imholt, T., Huang, J., Wheeler, K., Bonilla, A., Suresh, S. and Ortiz, C. (2010) Protection mechanism of the iron-plated armour of deep-sea hydrothermal vent gastropod. *Proceedings of the National Academy of Sciences of the United States of America*, 107, 987–992.

8
Smart technology for personal protective equipment and clothing

H. CAO, University of Delaware, USA

Abstract: This chapter reviews personal protective equipment (PPE) and clothing for different occupations and users, e.g., hazardous material (HAZMAT) workers, firefighters, industrial workers, healthcare personnel, and law enforcement and military personnel. The standards, requirements and commercial products for these PPE are discussed. The chapter covers the various types of smart technology that can be incorporated into textiles and clothing for personal protection, and applications and examples of smart PPE, including academic and industrial research and development, and commercial products. Future trends of smart PPE and helpful literature and websites are also included in this chapter.

Keywords: hazardous materials (HAZMAT), firefighter, welder, law enforcement, military, healthcare, active noise reduction, electronic circuits.

8.1 Introduction

According to the U.S. Occupational Health and Safety Administration (OSHA) definition (OSHA, 2006), personal protective equipment (PPE) 'is designed to protect workers from serious workplace injuries or illnesses resulting from contact with chemical, radiological, physical, electrical, mechanical, or other workplace hazards.' First responders, emergency service personnel, military personnel, and workers in specific occupations who may work in environments with chemical, biological, radiological, and nuclear (CBRN) materials, fire, and heat are required to wear specialized PPE. The purpose of wearing PPE, including gloves, foot and eye protection, protective hearing devices (earplugs, muffs), head protection, respirators and full body suits, is to minimize exposure to a variety of hazards (OSHA, 2003).

Based on different types of possible hazards that a person may encounter, PPE products will have different requirements, and are regulated by different government agencies or international nonprofit organizations. In the United States, OSHA, a unit in the Department of Labor, publishes the most comprehensive standards for workplace PPE required in general industry (29 CFR 1910), shipyard employment (29 CFR 1915), marine terminals (29 CFR 1917), longshoring (29 CFR 1918), and construction (29 CFR 1926).

For personnel who may be near the site of hazardous vapors, gases, and particles, U.S. Environmental Protection Agency (EPA) defines four levels of PPE protection, with level A required for the greatest protection and level D required for the minimum level of protection (EPA, n.d.). The EPA levels of protection are widely used by government agencies such as OSHA as well as PPE manufacturers. American National Standards Institute (ANSI), a private non-profit organization, has been developing safety standards since the 1920s. OSHA requires that many categories of PPE meet or be equivalent to standards developed by the ANSI. For instance, OSHA requires that PPE for eye and face protection meets ANSI Z87.1-1989 standard; PPE for head protection meets ANSI Z89.1-1986 standard; and PPE for foot protection meets ANSI Z41.1-1991 standard (OSHA, 2003). The International Safety Equipment Association (ISEA, www.safetyequipment.org) is the trade association for PPE manufacturers. As an accredited member of ANSI, ISEA's product groups draft PPE standards for public review and then for approval as American National Standards.

The National Fire Protection Association (NFPA), an international nonprofit organization, publishes Standards for Fire Departments on Occupational Safety and Health Programs (NFPA 1500). The first edition of NFPA 1500 standard was published in 1987, and the revised editions were published in 1992, 1997, 2002 and 2007. Before the introduction of NFPA 1500 standard, fire service organizations relied on the regulations that were developed for general industry, which did not address firefighters' specific needs and concerns (Stull and Stull, 2008).

This chapter discusses various types of PPE and protective clothing, and the applications of smart clothing in PPE. Future trends of smart PPE and helpful literature and websites are also included.

8.2 Types of personal protective equipment and clothing

Based on the threats they may encounter, firefighters, hazardous material (HAZMAT) workers, law enforcement personnel, military personnel, and employees in certain types of occupations such as welders use different types of PPE.

8.2.1 PPE for HAZMAT workers

U.S. EPA's four levels of protection are very useful in selecting PPE for HAZMAT workers who may have chemical and/or biological risks. According to EPA (n.d.), 'Level A protection is required when the greatest potential for exposure to hazards exists, and when the greatest level of skin, respiratory, and eye protection is required. Level B protection is required under circumstances requiring the highest level of respiratory protection,

with lesser level of skin protection. At most abandoned outdoor hazardous waste sites, ambient atmospheric vapors or gas levels have not approached sufficiently high concentrations to warrant level A protection, level B protection is often adequate. Level C is required when the concentration and type of airborne substances is known and the criteria for using air purifying respirators are met. Level D protection is the minimum protection required. Level D protection may be sufficient when no contaminants are present or work operations preclude splashes, immersion, or the potential for unexpected inhalation or contact with hazardous levels of chemicals.' Since these four levels are mainly for chemical protection, polyolefin, such as DuPont (Wilmington, Delaware, www.dupont.com) Tyvek®, are commonly used materials for this type of protective clothing.

Both level A and level B protection require the same level of respiratory protection with self-contained breathing apparatus (SCBA) or positive pressure supplied air respirator with escape SCBA. International Safety Instruments (ISI, Lawrenceville, Georgia, www.avon-isi.com) is one of the leading SCBA manufacturers in the U.S. Their SCBA products include Viking Z7, Z3000, Z3100, Vanguard, and Frontier. While levels A and B protection require the same inner and outer chemical-resistant gloves and boots, they have different requirements in protective suits. Level A protection requires a totally encapsulated chemical and vapor protective suit, and level B protection includes face shield, hooded chemical resistant clothing, and coveralls. According to DuPont Personal Protection (n.d.), a leading PPE manufacturer, a level A suit is vapor protective against chemicals with a high vapor pressure, and toxic through skin absorption, or carcinogenic substances. A Level B suit is not gas tight and can be used to protect against chemicals that are not vapors or gases having skin toxicity or which are carcinogenic. DuPont™ TyChem® products include both level A and level B suits.

Branson *et al*. (2005) conducted a series of six focus-group studies with first responders in five cities in the U.S., and found that the level B suit was used much more frequently than the level A suit. Level B HAZMAT suits were used hundreds of times a year in responding to a variety of incidents, while level A suits were typically used less than five times a year. The study also found that heat and humidity build-up were serious problems for both level A and level B suits, and an ambient temperature above 15.6 °C (60 °F) can cause heat exhaustion when wearing either suit (Branson *et al*., 2005). To solve this problem, a team led by Branson developed two liquid cooling vest prototypes, and found that the two prototypes positively affected user's skin temperatures, sweat rate, microclimate temperature, humidity, perceived temperature and perceived humidity (Peksoz *et al*., 2006).

Similar chemical protective suits, gloves and boots can be used for both level B and level C protection. However, SCBA is used for respiratory

protection in level B protection, while level C protection requires an air-purifying respirator that uses an air purifying filter, cartridge, or canister to remove air contaminants. Examples of air-purifying respirators include the 6000 series, 7500 series, and 7800 series respirators manufactured by 3M Corp (Maplewood, Minnesota, www.3m.com). No respiratory protection and limited skin protection are provided in level D protection. Level D PPE may include gloves, coveralls, safety glasses, face shield and boots.

8.2.2 PPE for firefighters

Firefighters require the best PPE available because of the nature of their jobs and the environment in which they perform their duties. A firefighter's full protective equipment for structural firefighting consists of personal protective clothing (helmet, protective hood, protective coat and trousers, gloves, safety shoes or boots, eye protection goggles or face shields, hearing protection), personal breathing apparatus SCBA, and personal alert safety system (PASS) (IFSTA, 1992). Good protective clothing and breathing apparatus can reduce and prevent injuries from fire, heat, smoke, oxygen deficiency and toxic atmospheres.

In the U.S., the same group of people may do both fire fighting and HAZMAT material cleaning jobs. Some PPE units such as SCBA may be used for both firefighters and HAZMAT workers. For instance, ISI's top of the line SCBA Viking 7 is National Institute for Occupational Safety and Health (NIOSH), CBRN, and NFPA compliant. The main difference between firefighter PPE and HAZMAT PPE is in the protective suit. Firefighters' main risk comes from fires, and their working environment may be extremely hot. In addition, a large quantity of high pressure water is used by firefighters during their work. Therefore, a firefighter's turnout gear, or bunker gear (coat and trousers), typically has three layers, namely a fire-resistant and water-resistant outer shell to protect against fires, a middle thermal insulation layer to protect against heat, and an inner layer moisture barrier to protect against water. Fire resistance properties are typically required for every layer of the bunker gear. FireDex LLC (Medina, Ohio, www.firedex.com) manufactured customizable gear FX™ that allows customers to choose fabrics for each layer. In FX™ products, fire resistant fibers used in the outer shell include the aramids Nomex® and Kevlar®, polyimide P84®, melamine fiber Basofil®, PBI®, and others. Quilt batting using the above-mentioned flame resistant fibers or a combination of flame resistant fibers and other thermal protection such as Caldura® can be selected as the thermal insulation liner. The moisture barrier could be ePTFE such as Stedair®, Crosstech®, and Gore® RT7100 on fire resistant Nomex®.

8.2.3 PPE for industrial workers

Many industrial sectors such as mining, welding and cutting, and construction require PPE for body protection, eye and face protection, hand protection, hearing protection, and head protection. Workers in different industrial occupations may encounter different types of threats, and thus need different types of PPE for protection. According to OSHA (2003), cooperative efforts of both employers and employees are needed for the greatest possible protection. It is the employers' responsibility to assess workplace hazards; identify, provide, maintain, and replace appropriate PPE for employees; train employees for using and caring for PPE; and periodically review, update and evaluate the effectiveness of the PPE program. It is the employees' responsibility to attend the PPE training session; care for and clean the PPE; and inform a supervisor the need for repair or replacement of the PPE.

ANSI Z89.1 is the PPE standard for head protection. There are two types of head protection: Type I helmet provides protection strictly from blows to the top of the head; and Type II helmet provides protection from blows to both the top and sides of the head. Under Z89.1-1997, three classes of helmets are categorized, based on electrical insulation: Class G (General, equivalent to Class A under Z89.1-1986 standard) for low voltage electrical protection (tested at 2200 volts); Class E (Electrical, equivalent to Class A under Z89.1-1986) for high voltage electrical protection (tested at 20 000 volts); and Class C (Conductive, equivalent to Class C under Z89.1-1986) with no electrical protection. For instance, Bullard (Cynthia, Kentucky, www.bullard.com) produces the Advent protective hat that provides Type II, Class E and G protection. Bullard's Standard Series Model S62 protective hat provides Class C protection.

ANSI Z87.1 is the PPE standard for face and eye protection that includes spectacles (plano and prescription), goggles, face shields, welding helmet, and full facepiece respirators to protect against workplace hazards such as impact, optical radiation, droplet and splash, dust, and fine dust particles (ISEA, n.d. a). ANSI Z41 was the PPE standard for foot protection but was superseded by American Society of Testing and Materials (ASTM) standard F2413 in 2005. ASTM F2413 (Standard Specification for Performance Requirements for Protective (Safety) Toe Cap Footwear) specifies the protective footwear requirements for impact resistance and compression resistance in the toe area, metatarsal protection, electrically conductive properties to reduce hazards from static electricity build-up and possibilities of ignition of explosives and volatile chemicals, electric shock protection, static dissipative (SD) properties, puncture resistance of footwear bottoms, chain saw cut resistance, and dielectric insulation. ANSI/ISEA 105–2011 standard was developed by ISEA's Hand Protection Group for

gloves, mittens, partial glove, or other hand protection equipment. The performance and pass/fail criteria against hazards such as cut, puncture and abrasion resistance, chemical permeation and degradation, detection of holes, vibration reduction, and heat and flame resistance are covered in the standard (ISEA, n.d. b). This standard does not address protection for welding, emergency response applications or fire fighter applications (ANSI, n.d.).

According to OSHA (n.d.), noise-related hearing loss has been one of the most prevalent occupational health concerns in the U.S. for more than 25 years. In 2009, the Bureau of Labor Statistics (BLS) reported more than 21 000 hearing loss cases due to high workplace noise level. OSHA sets legal limits on noise exposure in the workplace. These limits are based on a worker's time-weighted average over an eight-hour day. With noise, OSHA's permissible exposure limit (PEL) is 90 dBA for all workers for an eight-hour day. When the noise level is increased by 5 dBA, the amount of time a person can be exposed to a certain noise level to receive the same dose is cut in half (OSHA, n.d.). This means that OSHA allows 4 hours of exposure to 95 dBA sound level, and 2 hours of exposure to 100 dBA sound level. Hearing protection devices include single-use earplugs made of waxed cotton, foam, silicone rubber or fiberglass wool, molded earplugs that must be individually fitted by a professional, and earmuffs (OSHA, 2003).

8.2.4 PPE for healthcare personnel

The greatest threat a healthcare employee may encounter comes from infectious materials. PPE that protects healthcare employees against infectious materials include gloves, gowns, masks, goggles, and respirators. The U.S. Center for Disease Control and Prevention (CDC) provides very helpful guidance for selecting and using PPE for healthcare workers (CDC, n.d.). Fit and comfort are important in healthcare PPE. Healthcare gloves need to fit the hands comfortably and be durable for several hours of use. Common materials for gloves are vinyl, latex, and nitrile. Gowns are usually made from cotton and spun synthetic fibers for comfort purpose. A fluid resistance gown may be used if a fluid penetration threat exists. To ensure protection, the long sleeves of gown, mask, and goggles should fit snuggly at the wrists, over the mouth and nose, and over and around the eyes, respectively. A respirator that filters air before inhaling, or a powered air-purifying respirator if there is an existing higher level of respiratory threat, is used to protect healthcare providers against hazardous and infectious aerosols. Sterile gloves and gowns are necessary in invasive procedures to further protect patients, as well as healthcare providers (CDC, n.d.).

Proper use of PPE is critical for the safety of healthcare providers and patients, and CDC (n.d.) has published detailed guidance for how to don,

use and doff PPE to prevent disease transmission. However, it is a challenge for a healthcare provider to always comply with the requirements. Beam *et al*. (2011) studied the PPE usage behavior of ten registered nurses, respiratory therapists, and nursing assistants in a simulated healthcare environment and found that each of the ten participants committed at least one breach of standard airborne and contact isolation precautions. Not conducting a seal check and not tying the gown at both the neck and the waist were among the most common breaches in PPE donning. Not using proper mask removal technique and using poor technique for gown removal were among the most common breaches in PPE doffing. Not donning and doffing PPE in CDC-recommended sequence were also very common, with 7 out 10 not donning, and 9 out of 10 not doffing, in the proper sequence (Beam *et al*., 2011).

8.2.5 PPE for law enforcement and military personnel

Body armor that can protect the wearer against ballistic weapons is the most commonly used PPE for law enforcement and military personnel. For law enforcement armors, National Institute of Justice (NIJ) Standard 0101.04, Ballistic Resistance of Personal Body Armor, specifies seven classes of protection against ballistic threat, depending on bullet composition, shape, caliber, mass, angle of incidence, and impact velocity (NIJ, 2001). They are Type I for .22 caliber Long Rifle Lead Round Nose (LR LRN) bullets and 380 ACP Full Metal Jacketed Round Nose (FMJ RN) bullets; Type IIA for lower velocity 9 mm and 40 S&W ammunition; Type II for high velocity 357 Magnum and higher velocity 9 mm ammunition; Type IIIA for high velocity 9 mm and 44 Magnum ammunition; Type III for rifles; Type IV for armor piercing rifles; and Special Type for a level of protection other than one of the above standard types (NIJ, 2001).

Type I armor provides the minimum protection that any officer should have and Type IIIA armor is suitable for routine wear in many situations. Soft armors, made from many layers of woven or laminated fibers, are capable of providing Types I to IIIA protection. According to NIJ (2004), more than 65 manufacturers worldwide have submitted armor to NIJ to validate their armor's performance in accordance with the NIJ body armor standard. DuPont (Kevlar® fiber), Honeywell (Spectra® fiber), Teijin Twaron (Twaron®), DSM (Dyneema®), and Toyobo (Zylon®) are the predominant ballistic material producers for soft armor (NIJ, 2004). Kevlar® and Twaron® are aramids, Spectra® and Dyneema® are highly oriented polyethylene, and Zylon® is polybenzobisoxazole (PBO) (Phoenix and Porwal, 2003).

Types III and IV armors are used only in tactical situations, when the threat warrants such protection (NIJ, 2001). Soft vests reinforced with metal or ceramic plates are typically used for protecting law enforcement

personnel against rifle rounds (Type III and Type IV), and for military personnel. Due to the weight and rigidity of metal and ceramic plates, plate-reinforced hard armor is usually used for torso protection (vest). To protect limbs of combat soldiers against improvised explosive devices (IEDs), Matic *et al.* (2006) developed QuadGard® arm and leg protection armor that have been used by U.S. Marine Corps, Army, Air Force and Navy units. QuadGard®, weighing only 10 pounds, uses lightweight and soft ballistic materials to provide extremity protection against fragments from conventional munitions and IEDs. The testing and evaluation with warfighters showed that it achieved a high level of acceptance for its flexibility and comfort (Matic *et al.*, 2006).

8.3 Applications of smart clothing in personal protective equipment

In materials and structures, 'smart' is defined as sensing and reacting to environmental conditions or stimuli, such as those from mechanical, thermal, chemical, electrical, magnetic or other sources (Tao, 2001). Smart clothing uses clothing as the platform for micro-processors, electronic devices, sensors and communication devices, so it can sense and react to environmental conditions or stimuli, and provide an enhanced environmental and personal awareness. Advances in miniaturization, new sensors, computing science and related technologies have resulted in the emergence of smart clothing (Axisa *et al.*, 2005). Electronic devices can be integrated in any unit of PPE, such as suit, gloves, head and foot protection, and respirator.

8.3.1 Smart PPE for industrial protection

Buchweiller *et al.* (2003) mentioned a few integrations of electronics in PPE during the earlier years. In 1973, Gordon (1975) filed a U.S. Patent (3,873,804) that integrated a liquid crystal display together with an electric circuit into the eye piece of a welding helmet for optical protection. As claimed in this patent, the helmet 'requires nothing from [the welder] except that he puts on the helmet and may then go about his work. He does not have to operate a separate switch or any other piece of equipment. He merely picks up his electrode and this invention (helmet) protects his eyes solely upon approach of his electrode to the workpiece.' This invention was one of the earliest smart technology applications in PPE.

The technology of active noise reduction (ANR), also known as active noise control or noise cancellation, is a technology to reduce unwanted sound by emitting a sound wave with the same amplitude but inverted phase to the noise. Due to its long wavelength, low frequency noise can

travel great distances and penetrate passive barriers such as cement walls, which makes it very difficult to attenuate. Pro Tech Technologies Inc. (Wilton, Connecticut, www.noisebuster.net) incorporated ANR technology into a PPE application and developed NoiseBuster® ANR Safety Earmuff. The NoiseBuster® ANR earmuff uses a microphone in the ear cup to capture the noise, electronically create an anti-noise wave that is identical to the noise but opposite in phase, and output the anti-noise wave through a speaker that is also located in the ear cup. The NoiseBuster® ANR earmuff combines passive noise reduction up to 26 dB and electronic active noise reduction up to 20 dB, to provide very effective protection against noise. The NoiseBuster® ANR earmuff is available in three models: over-the-head, behind-the-head, and hard hat cap mount, and can protect employees in many professions such as pipeline workers, assembly line workers, airplane maintenance workers, and coal miners.

8.3.2 Smart PPE for firefighters

The personal alert safety system (PASS) device, about the size of a portable transistor radio worn on the firefighter's SCBA or coat, is mandatory for all firefighters under NFPA 1500 (Standard on Fire Department Occupational Safety and Health Program). PASS uses a motion detector to sense a firefighter's movement or lack of movement and will emit a loud, pulsating shriek if a firefighter collapses or remains motionless for approximately 30 seconds (IFSTA, 1992). It can be considered as one of a few smart PPE devices that are approved and required by an international PPE standard. Caught or trapped has always been one of the leading causes for firefighter on-duty deaths. The most recent NFPA report (Fahy *et al.*, 2011) found that in 2010, eight firefighters died from being caught or trapped, which is the third leading cause for a total of 72 firefighter on-duty deaths. If properly implemented, the PASS device can serve as a platform for the incorporation of additional and more innovative technology to help reduce fatalities and injuries resulting from caught or trapped firefighters (Bryner *et al.*, 2005). Tests performed by the Mesa (Arizona) Fire Department showed that locating even the loud shriek of a PASS device in poor visibility conditions can be more difficult than expected. The reasons include sound reflecting from walls, ceilings, and floors; noise from SCBA operation; and muffled hearing due to protective hoods (IFSTA, 1992).

As indicated previously, firefighters' protective clothing effectively insulates them from the thermal environment around them. Due to the thermal insulation, sometimes it is difficult for the firefighters to appreciate how much heat flux they have been exposed to during fire fighting operations. The thermal environment can range from slightly elevated temperatures, 66 °C, in which firefighters may be able to work for longer periods, up to

pre-flashover temperatures, 650 °C, in which firefighters must quickly escape. Currently, thermal sensors are incorporated into many PASS devices to warn firefighters of a range of thermal exposures (Bryner *et al*., 2005). Viking Life Saving Equipment (Esbjerg, Demark, www.viking-life.com) have developed an NFPA compliant intelligent garment that integrates thermal sensors in the inner and outer layers of a firefighter coat, and the sensors are connected to LED displays on the sleeve and back of the left shoulder. The sensors can monitor heat near the firefighter and outside the coat. The LED displays can alert the firefighter to critical temperatures that cause heat stress and burn. The LED on the lower sleeve indicates elevated temperatures both inside and outside of the coat: flashing slowly when external temperatures reach about 250 °C or the internal temperature reaches about 50 °C, and flashing rapidly when external temperatures reach about 350 °C or the internal temperature reaches about 68 °C. The shoulder LED display of Viking's intelligent clothing is also visible to other firefighters, alerting them to a potentially dangerous thermal environment.

Sudden cardiac death has always been the leading cause for U.S. firefighter on-duty fatalities. In 2010, 35 firefighters died from sudden cardiac death, which accounts for 49% of the total 72 firefighter on-duty deaths (Fahy *et al*., 2011). From 1995 through 2004, 449 firefighters, or almost half of the total number of fire fighters who died while on duty, fell victim to sudden cardiac deaths (Fahy, 2005). To monitor a firefighter's heart health as well as thermal environment, Peksoz *et al*. (2009) developed smart firefighter clothing prototypes by incorporating a wireless sensor network (WSN) into the firefighter's coat and glove. A WSN is composed of many sensor nodes, also called motes, for sensing and communication. The basic components in a sensor mote include an embedded microprocessor, a memory with limited capacity, a low-power radio for communication and a battery. In the smart firefighter clothing prototypes developed by Peksoz *et al*. (2009), the WSN was based on the Mica sensor motes produced by Crossbow Technology Inc. (San Jose, CA, www.xbow.com). The Mica sensor mote and mote-based pulse oximeter devices, including finger sensor, oximeter board, and connection board, were incorporated into a firefighter glove to monitor a firefighter's heart rate and blood oxygen saturation, and wirelessly send the data to a remote computer (Peksoz *et al*., 2009). Two sets of stacked Mica sensor mote and environmental sensor board that have the capacity of measuring temperature and relative humidity were placed in sensor receptacles attached to the center back and left side of the chest in the moisture barrier inner lining of the coat, to monitor the microclimate temperature and humidity. A third set of stacked Mica sensor mote and environmental sensor board was placed in an exterior pocket made from one layer of outer shell fabric of the firefighter coat, to monitor ambient conditions (Peksoz *et al*., 2009).

8.3.3 e-Textiles and smart PPE for military personnel

A lot of smart clothing is based on electronic textiles (e-textiles) (Marculescu *et al*., 2003), in which conductive metal or polymer fibers are embedded in fabrics to serve as electrical circuits. The methods to embed conductive fibers into textile fabrics include weaving (Martin *et al*., 2004; Park and Jayaraman 2001), knitting (Paradiso *et al*., 2005) and embroidering (Post *et al*., 2000). Plain weave, the most elementary and simple textile structure, provides a tight mesh of individually addressable insulated metal filaments that can be used as basic transmission lines or whole circuits (Marculescu *et al*., 2003). The Georgia Tech Wearable Motherboard (GTWM™) (Park and Jayaraman 2004), one of the earliest e-textiles, is an example of this woven architecture of a textile-based computer motherboard for special purpose chips and processors. As indicated on the GTWM™ website (GTWM, n.d.), the wearable motherboard served as a flexible information infrastructure and a system for monitoring the vital signs of individuals. The third generation of GTWM™ was a smart shirt in which the plastic optical fiber (POF) was spirally integrated into a single-piece undershirt during the fabric weaving process. It was the first woven full-fashion garment with no 'cut and sew' operations, so the POF does not have any discontinuities at the armhole or the seams. Sensors, such as electrocardiogram (EKG) sensors, can be connected to the smart shirt and vital sign data such as temperature, heart rate, and respiration rate, and information about wounds, can be collected and transmitted to monitoring equipment or DARPA's (Defense Advanced Research Projects Agency) personal status monitor. The GTWM™ project was funded by the U.S. Department of Navy, so the original application was for military protection, but the wearable information infrastructure can be easily customized for applications in personalized information processing, healthcare and telemedicine, space exploration, and others (GTWM, n.d.).

Other woven e-textile research can be found in Virginia Polytechnic Institute and State University (Virginia Tech) (Martin *et al*., 2004) and Carnegie Mellon University (Stanley-Marbell *et al*., 2003). e-Textiles have three common design goals: low cost, durability and long running (Marculescu *et al*., 2003). Inexpensive, off-the-shelf electronic components are often used in e-textiles to ensure low manufacturing costs. The communication among processing elements is by wired in e-textiles. This is more power efficient than wireless communications (Marculescu *et al*., 2003). It was found that energy consumption of wireless communication is about 14 times that of wired communication (Jones *et al*., 2003). The low energy consumption in communication ensures long running of e-textiles. Durability is often a concern for the wired communication e-textiles. Because of manufacturing defects, and normal wear and tear on the fabric, it is likely that wires

will be broken or shorted in the e-textile over the course of its lifetime (Martin *et al*., 2004). Several fault tolerance research studies (Martin *et al*., 2004; Stanley-Marbell *et al*., 2003) have been conducted to improve the durability and reliability of e-textiles; however, e-textiles still have higher failure rates than non-textile based sensor networks (Marculescu *et al*., 2003).

8.4 Conclusion and future trends

The production, use and maintenance of PPE are highly regulated, with numerous national, multi-national, and international standards. The application of smart technology or integration of electronics in PPE is still relatively new. Improving user safety is the most important purpose for PPE and safety should never be impaired in any PPE. However, none of the existing standards has dealt with the safety aspect of integrating electronics into PPE. Buchweiller *et al*. (2003) indicated that no methodology has been developed to answer the safety questions arising from integrating electronic circuits into PPE, and proposed a new method to address this issue. To make smart clothing succeed in the PPE market, a safety assessment methodology for different PPE products must be developed. Following the assessment methodology, the standards for smart PPE need be developed and approved by government agencies, international nonprofit organizations, or industrial trade associations.

Buchweiller *et al*. (2003) raised a few questions on the level of protection, confidence and reliability, and new risks associated with integrating electronics into PPE. The future design and development of smart PPE must address these questions. Smart PPE should provide an equivalent level of protection to traditional PPE, and smart PPE standards must meet the same safety criteria as the existing PPE standards. Smart PPE should provide sufficient reliability for the lifetime of the product. The application and environment should not adversely affect the reliability of the electronic circuits or devices used in PPE. This is extremely important for PPE used in hostile environments, such as firefighter's PPE. For example, in firefighter's PPE, the electronic circuits or devices may need to be protected against water, fire or heat, so they will not fail during use. The incorporation of electronic devices should not introduce new risks, especially in hostile environments.

The design of smart PPE must assure easy use and maintenance. Some PPE users such as HAZMAT workers or firefighters have a very short time to don their PPE, so that they can have the quickest response time to an incident. This requires that the electronic devices be seamlessly integrated into PPE and that the smart PPE does not require a complicated calibration or 'turn-on' procedure. Some electronic devices may need to be removed

from PPE during maintenance, cleaning, or care. After that, they must be capable of being easily returned to their correct position by the users.

8.5 Sources of further information and advice

- OSHA's general overview on PPE can be found at www.osha.gov/Publications/osha3151.pdf.
- PPE guidance for welding and cutting professionals can be found at www.aws.org/technical/facts/FACT-33.pdf. U.S.
- CDC guidance on PPE selection, and use in healthcare setting can be found at www.cdc.gov/HAI/pdfs/ppe/PPEslides6-29-04.pdf.
- Most of the leading PPE manufacturers are member companies of International Safety Equipment Association (ISEA). The ISEA website www.safetyequipment.org has useful information on PPE.
- The 'PPE Update' column in FireRescue1.com by Jeffery and Grace Stull provides a useful summary of firefighter PPE. These articles can be found at www.firerescue1.com/Columnists/Jeffrey-O-Stull/.

8.6 References

ANSI (American National Standards Institute) (n.d.). ANSI/ISEA 105, http://webstore.ansi.org/RecordDetail.aspx?sku=ANSI/ISEA+105-2011, accessed on September 22, 2011.

Axisa, F., Schmitt, P. M., Gehin, C., Delhomme, G., McAdams, E., Dittmar, A. (2005). Flexible technologies and smart clothing for citizen medicine, home healthcare, and disease prevention. *IEEE Transactions on Information Technology in Biomedicine, 9*(3), 325–336.

Beam, E. L., Gibbs, S. G., Boulter, K. C., Beckerdite, M. E., Smith, P. W. (2011). A method for evaluating healthcare workers' personal protective equipment technique. *American Journal of Infection Control, 39*(5), 415–420.

Branson, D. H., Farr, C. A., Peksoz, S., Nam, J., Cao, H. (2005). Development of a prototype personal cooling system for first responders: user input. *Journal of ASTM International*, *2*(2), Paper ID: JAI12105.

Bryner, N., Madrzykowski, D., Stroup, D. (2005). Performance of thermal exposure sensors in personal alert safety system (PASS) devices, *National Institute of Standards and Technology Report NISTIR 7294*. http://www.fire.nist.gov/bfrlpubs/NIST_IR_7294.pdf, accessed on September 25, 2011.

Buchweiller, J.-P., Mayer, A., Klein, R., Iotti, J.-M., Kusy, A., Reinert, D., Christ, E. (2003). Safety of electronic circuits integrated into personal protective equipment (PPE). *Safety Science, 41*, 395–408.

CDC (Centers for Disease Control and Prevention) (n.d.). *Guidance for Selection and Use of Personal Protective Equipment (PPE) in Healthcare Settings*, http://www.cdc.gov/HAI/pdfs/ppe/PPEslides6-29-04.pdf, accessed on September 15, 2011.

DuPont Personal Protection (n.d.). *Glossary: Industrial*, http://www2.dupont.com/Personal_Protection/en_US/tech_info/glossary_industrial.html, accessed on September 20, 2011.

EPA (Environmental Protection Agency) (n.d.). *Personal Protective Equipment*, http://epa.gov/osweroe1/content/hazsubs/equip.htm, accessed on September 28, 2011.

Fahy, R. F. (June, 2005). *U.S. firefighter sudden fatalities due to sudden cardiac death*, 1995–2004, http://www.nfpa.org/assets/files/PDF/OSCardiacDeath.pdf, accessed on October 2, 2011.

Fahy, R. F., LeBlanc, P. R., Molis, J. R. (June/July, 2011). *Firefighter Fatalities in the United States – 2010*, http://www.nfpa.org/assets/files/PDF/osfff.pdf, accessed on October 1, 2011.

Gordon, M. (1975, March). *Welding Helmet with Eye Piece Control*. US Patent 3,873,804.

GTWM (*Georgia Tech Wearable Motherboard)* (n d.), http://www.gtwm.gatech.edu/, accessed on September 23, 2011.

IFSTA (International Fire Service Training Association) (1992). *Essentials of fire fighting*, Fire Protection Publications (3rd Edition), Oklahoma State University, Stillwater, OK.

ISEA (International Safety and Equipment Association) (n.d. a) ANSI/ISEA Z87.1-2010, http://www.safetyequipment.org/c/stdz871-2010.cfm, accessed on September 30, 2011.

ISEA (International Safety and Equipment Association) (n.d. b) ANSI/ISEA 105–2011, http://www.safetyequipment.org/c/std105-2011.cfm, accessed on September 30, 2011.

Jones, M., Martin, T., Nakad, Z., Shenoy, R., Sheikh, T., Lehn, D., Edmison, J. (2003). Analyzing the use of e-textiles to improve application performance. *IEEE Vehicular Technology Conference 2003, Symposium on Wireless Ad hoc, Sensor, and Wearable Networks (VTC 2003)* (extended abstract), October 2003.

Marculescu, D., Marculescu, R., Zamora, N. H., Stanley-Marbell, P., Khosla, P., Park, S., Jayaraman, S., Jung, S., Lauterbach, C., Weber, W., Kirstein, T., Cottet, D., Grzyb, J., Troster, G., Jones, M., Martin, T., Nakad, Z. (2003). Electronic textiles: a platform for pervasive computing, *Proceedings of IEEE, 91*(12), 1995–2018.

Martin, T., Jones, M., Edmison, J., Sheikh, T., Nakad, Z. (2004). Modeling and simulating electronic textile applications. *Proceedings of the ACM SIGPLAN/SIGBED Conference on Languages, Compilers, and Tools for Embedded Systems (LCTES '04)*, June 11–13, 2004, Washington, DC, 10–19.

Matic, P., Hubler, G. K., Sprague, J. A., Simmonds, K. E., Rupert, N. L., Bruno, R. S., Frost, J. J., Branson, D. H., Farr, C., Peksoz, S. (2006), QuadGard arm and leg protection against IEDs, *NRL Review*, 73–81. http://www.nrl.navy.mil/content_images/06FA3.pdf, accessed on September 30, 2011.

NIJ (National Institute of Justice) (2001, June). NIJ Standard-0101.04: *Ballistic Resistance of Personal Body Armor*, http://www.justnet.org/Lists/JUSTNET%20Resources/Attachments/758/0101.04RevA.pdf, accessed on September 23, 2011.

NIJ (National Institute of Justice) (2004, March). *Special Report: Status Report to the Attorney General on Body Armor Safety Initiative Testing and Activities*, http://www.ojp.usdoj.gov/bvpbasi/docs/ArmorReportWithPress.pdf, accessed on September 20, 2011.

OSHA (Occupational Safety and Health Administration) (2006, April). OSHA® fact sheet: *Personal Protective Equipment*, http://www.osha.gov/OshDoc/data_General_Facts/ppe-factsheet.pdf, accessed on September 30, 2011.

OSHA (Occupational Safety and Health Administration) (2003). *Personal Protective Equipment*, http://www.osha.gov/Publications/osha3151.pdf, accessed on September 28, 2011.

OSHA (Occupational Safety and Health Administration) (n .d.). *Occupational Noise Exposure*, http://www.osha.gov/SLTC/noisehearingconservation/, accessed on September 30, 2011.

Paradiso, R., Loriga, G., Taccini, N. (2005). A wearable health care system based on knitted integrated sensors. *IEEE Transactions on Information Technology in Biomedicine, 9*(3), 337–344.

Park, S., Jayaraman, S. (2001). Adaptive and responsive textile structures. In *Smart Fibers, Fabrics and Clothing*, X. Tao (ed.), Woodhead Publishing, Cambridge, UK, 226–245.

Park, S., Jayaraman, S. (2004). e-Health and quality of life: the role of the wearable motherboard. In *Wearable eHealth Systems for Personalised Health Management*, A. Lymberis and D. de Rossi (eds.), IOS Press, Amsterdam, The Netherlands, 239–252.

Peksoz, S., Branson, D., Cao, H., Jacobson, B., Farr, C., Nam, J. (2006). Evaluation of two liquid cooled prototype vests through human subject testing. *Research Journal of Textile and Apparel*, *10*(3), 17–27.

Peksoz, S., Park, H., An, S. K., Cao, H. (2009). Smart clothing for firefighter protection. *Proceedings of the Intelligent Textiles and Mass Customization International Conference*, Casablanca, Morocco, November 2009.

Phoenix, S. L., Porwal, P. K. (2003). A new membrane model for the ballistic impact response and V_{50} performance of multi-ply fibrous systems. *International Journal of Solids and Structures, 40*, 6723–6765.

Post E. R., Orth, M., Russo, P. R., Gershenfeld, N. (2000). E-broidery: design and fabrication of textile-based computing. *IBM Systems Journal, 39*(3&4), 840–860.

Stanley-Marbell, P., Marculescu, D., Marculescu, R., Khosla, P. (2003). Modeling, analysis, and self-management of electronic textiles. *IEEE Transactions on Computers, 52*(8), 996–1010.

Stull, J. O., Stull, G. G. (2008). *How NFPA 1500 Applies to Firefighter PPE*, http://www.firerescue1.com/fire-products/Personal-protective-equipment-ppe/articles/405678-How-NFPA-1500-Applies-to-Firefighter-PPE/, accessed on October 3, 2011.

Tao, X. (2001). Smart technology for textiles and clothing: introduction and overview. In *Smart Fibers, Fabrics and Clothing*, X. Tao (ed.), Woodhead Publishing, Cambridge, UK, 1–6.

9
Smart protective textiles for older people

J. McCANN, University of Wales, Newport, UK

Abstract: This chapter considers the application of smart textiles and wearable technologies to enhance the functionality of a multi-purpose, protective 'clothing layering system' for the benefit of older people. Little has been done to address physical and cognitive limitations when developing smart textile products and services appropriate to the real-world needs and aspirations of active older users. The author looks at how the appropriate design of smart clothes has the potential to promote independence and wellbeing, and may enable participation in healthy exercise in the everyday lives of the active ageing.

Key words: smart clothes, layering, active ageing, older people.

9.1 Introduction

There is a lack of understanding of the actual and potential role of wearable technological advances in everyday lives of older people, and developments have often failed to address their aspirations. As technical textiles merge with wearable electronics and information communications technologies, many textile-based products have been developed with little concern for aesthetic appearance, comfort and ease of use. Such advances may be utilised to promote health and wellbeing but may not be readily accepted by some older users due to badly designed user-interfaces that have small controls or displays that may prevent someone with a minor impairment from using them effectively. Little has been done to address physical and cognitive limitations when developing these new products and services to ensure that they are appropriate to the real-world needs of older users.

This chapter considers design innovations in smart textiles and wearable electronics that may be introduced into the various layers within a functional clothing system, with the potential to protect and enhance the autonomy, independence and wellbeing of older people. As Huppert (2003) explains 'Simple alterations in the design process and its outputs will attract the growing body of older consumers, and result in older people, in general, leading more fulfilled and independent lives, to the benefit of individuals, families and the society at large'.

The author recognises that design practitioners must be central to the future cross-disciplinary product development team, in addressing design

requirements for the protection of the ageing, related to the demands of their lifestyles. This chapter introduces design challenges to do with the changing ageing body and describes a range of textiles and applications in a shared language that may be understood by designers, older people, their families, and their carers, in order to introduce textile-based products, enhanced with unobtrusive assistive technology, with controls that are easy to operate, to older people who will willingly wear and enjoy them.

9.2 The demands of the changing body

9.2.1 The active ageing

The ageing community may be segmented as the Active Ageing, approximately 60–75, and as fourth age, for people over 75, or those who are dependent on care. 'We are now living in a unique historical period. Never before could people expect to live so long. Never before have physical and mental capabilities remained so high into advanced old age' (Huppert, 2003). Today, the average age of death in the UK is around 80, with diseases and impairments often rare until advanced old age. However, our images and expectations of ageing are derived from the way in which individuals aged in the past. Older people today are fitter and more capable than in the past, and their capabilities are related to how actively they use them. 'Consumer research and marketing have failed to realize the relationship between changes in the leading values, views, and behaviours of the marketplace and the New Customer Majority' (Wolfe and Snyder, 2003). Clothing is a major contributor to how people define and perceive themselves and the 'Baby Boomer' generation has been accustomed to making choices in the design of their clothing throughout their lives, since their teenage years in the 1960s. Throughout this period, great innovation has taken place in technical textiles with, most recently, the emergence of smart textiles and wearable electronics, with the potential to enhance health and wellness, and offer a range of protection to the ageing body.

In terms of chronological age, certain physiological changes in the older body result in clothing that may be uncomfortable due to inappropriate fit, styling, proportion and weight, and also difficult to put on, take off and fasten. Much impairment is due to restricted levels of physical activity. 'Older people have the greatest need to maintain their exercise levels, and those with some disease related impairment may have the most to gain' (Metz and Underwood, 2005). Fall-related injuries are a major cause of pain, disability, loss of independence and premature death, with worldwide statistics reporting that approximately 28–35% of people aged of 65 and over fall each year, increasing to 32–42% for those over 70 years of age (World Health Organisation, 2007). 'There is growing evidence that keeping

fit and supple in old age is a good way to protect the body from a number of medical problems, such as high blood pressure, heart disease and osteoporosis, as well as helping to prevent falls and broken bones' (Metz and Underwood, 2005). 'It is a mistake to think of the older user as a wheelchair user or as severely disabled, hard of hearing or partially sighted. Older users are that vast number of people who, in advancing age, have little discernible impairment, but have a strong drive to remain independent and to contribute to the community, but are hampered by inappropriate design' (Huppert, 2003).

9.2.2 Monitoring vital signs

Vital signs include body temperature, respiratory rate, heart rate (pulse), and blood pressure, all of which may be observed, measured, and monitored to enable the assessment of the level at which an individual is functioning. Normal ranges of measurements are liable to change with age and medical conditions. Body temperature may be checked for any signs of systemic infection or inflammation in the presence of a fever or for hypothermia caused by prolonged exposure to low temperatures. Respiration rates and difficulty in breathing may increase with fever, illness, or other medical conditions. The pulse rate gradually decreases from birth to adulthood, then increases with advancing old age. The pulse rate will generally increase with elevation in body temperature and also as a result of pain, as well as with emotions, such as fear, anger, anxiety, and excitement.

High blood pressure, or arterial hypertension, can be an indicator of many problems and may have long-term adverse effects as a risk factor for strokes, heart attacks, heart failure and arterial aneurysms; and it is a leading cause of chronic renal failure. High blood pressure tends to increase as people get older, and even moderate elevation of arterial pressure leads to shortened life expectancy. Below the age of 55, men have a greater chance of having high blood pressure than women of a similar age, while women are more likely to have high blood pressure after the menopause than before. Some diseases lead to a disruption in the flow of fluids, leading to swelling in the legs, ankles and feet, known as oedema. A blockage of the lymphatic system, resulting from cancer or lymph gland inflammation, can also lead to leg and wrist swelling. Preventative lifestyle changes are recommended to ensure good cardiovascular health and help prevent the onset of disease, such as dietary changes, increased exercise, giving up smoking and losing weight.

Homeostasis, in relation to the thermal regulation of the ageing body, has a direct relationship to textile selection. In terms of protection of the clothing microclimate, clothing can impede evaporative heat transfer by disallowing movement of water vapour across the various layers, creating a

microenvironment next to the skin surface. The surface area coverage (and permeability) can determine the extent and nature of this microenvironment. As perspiration increases, there is a reduction in the capacity of evaporation to remove heat energy and this means that most of the sweat from the body becomes trapped within the fibres and textiles. Clothes saturated by sweat can affect the thermal characteristics and influence further heat transfer rates. Textiles may be selected to reduce the effects of sweating, through 'wicking away' moisture.

9.2.3 Physical performance

Physical exercise can improve physical performance in later life, as well as aspects of intellectual performance. Particular aspects that decline with age, and which are important for functioning, include mobility, dexterity and the ability to reach and stretch (Metz and Underwood, 2005). 'To perform physically at a level which ensures an independent lifestyle requires adequate muscle strength, muscle power, flexibility, balance and cardiorespiratory endurance' (Huppert, 2003). Muscle strength begins to decline quite sharply from around age 50. Hand strength, for those of 75+, is less than half of the value for young adults. Muscular strength is rarely used without movement, so muscular power (which combines strength and speed) is required in dynamic activities such as climbing stairs, rising from a chair, getting onto a bus or out of a bath. Muscle power tends to decline even more sharply than muscle strength (Huppert, 2003).

Physical capabilities are influenced by the size and shape of the body. From mid-adulthood, people begin to lose height, with the average height of 65–74 year olds being 5 cm less than the average height of those aged 16–24. This height difference is almost double for those aged 75+ (Department of Health 2002). Other bodily dimensions also change with advancing age; feet become broader, waistlines thicken as the ratio of body fat to muscle changes. Physical strength is generally related to body size, with women physically weaker than men at all ages, and with weaker muscles and a poorer power-to-weight ratio. Their disadvantage is even greater on weight-bearing activities, such as walking and stair climbing (Huppert, 2003).

Flexibility and adequate range of movement are essential for many activities, with loss of range, especially in the shoulder joint, common in old age. Arthritis causes swelling and pain in the joints, and limited movement and weakness in the arms and hands, resulting in poor dexterity and restricted flexibility while dressing and undressing, and difficulty in getting a firm grip or in making precise finger movements (Metz and Underwood, 2005). Double actions, such as push and twist, are particularly difficult for people with poor dexterity. Balance requires a complex integration of sensory

inputs followed speedily by precise motor reactions. To restore equilibrium of the body mass, to avoid falling after tripping, requires rapid powerful movements, and these decline with age, resulting in a greater tendency to fall (Huppert, 2003).

9.2.4 Sensory capabilities

'To obtain information about the world around us, we rely on our five main senses – vision, hearing, taste, smell and touch. Physiological changes occur in all our sense organs as we age, reducing our sensitivity to incoming information' (Huppert, 2003). As the lenses of the eyes lose some of their ability to accommodate, older people will find a decline in their ability to see detail, focus on near objects, discriminate differences between levels of contrast, adapt to changes in brightness, and manage in extremely bright light. A yellowing of the lens will cause impairment in colour perception. Older people will experience hearing loss that may cause problems in demanding listening situations, such as detecting faint sounds in the presence of background noise. Amplification can improve some aspects of hearing but those who are hard of hearing often show symptoms of depression and may become socially withdrawn or, alternatively, cope with their difficulty by doing most of the talking rather than struggling to listen (Huppert, 2003).

Perception of taste is intimately associated with sense of smell; different odorants stimulate different receptors at the back of the nose. There is little loss in ability to identify odours up until the age of about 65 but, beyond that age, impairment can be marked, affecting appetite regulation and food selection, reducing pleasure from fragrances and putting people at risk from an inability to detect dangerous smells, such as decaying foods or leaking gas. 'The skin, source of most of our tactile sensations, declines in sensitivity with age the same as other sensory receptors' (Wolfe and Snyder, 2003). Touch is a combination of the stimulation of three types of receptors on the skin: pressure, pain and heat/cold. As ageing skin receptors die off, hands become less sensitive to pressure. Points touching the skin need to be further apart for an older person to recognise two sources of pressure rather than one, leading to a reduced ability to differentiate between shapes and textures (Huppert, 2003).

9.2.5 Cognitive capabilities

'The ability to function independently is as much related to our mental capabilities as to our physical capabilities. The term cognition refers to the set of mental capabilities by which we pay attention to the world around us, interpret the information that comes in from our senses, learn and

remember, solve problems and make decisions' (Huppert, 2003). While mental capabilities decline, impairment may be evident only when elders face a situation that is novel, demanding or complex. Mental abilities, based on information acquired over long periods of time, tend to remain stable, whereas abilities that require the rapid assimilation and analysis of new information, tend to decline quite sharply. Cognitive ability is influenced by physical disorders, depression, medication, stress levels and amounts of sleep and, with ageing, these factors may increase cognitive impairment. However, '80% of those aged over 80 do not have dementia, and many of these individuals show little evidence of cognitive impairment even in their 90s and beyond' (Huppert, 2003). Learning and new experiences can result in the formation of new connections between brain cells, with 'use it or lose it' applying as much to the brain as to our muscles (Hultsch *et al.*, 1999).

When constantly bombarded by sensory information, people must be selective while, at the same time, monitoring other sources of information so as not to miss important or dangerous signals. The ability to sustain and shift attention between incoming sources decreases with age, especially when doing two or more things simultaneously. Literacy remains essential for understanding instructions, such as the functionality of electronic devices or taking medication, and in understanding information derived from print, internet, and street signs. Much information is verbal, although the meaning of symbols should be remembered to prompt appropriate actions. Numerical and calculation skills also decline while, 'at any age, our ability to understand numerical concepts and solve numerical problems depends on the way in which the information is presented' (Huppert, 2003). Visual–spatial abilities tend to decline significantly; for example, when walking or driving around a new environment or following a map.

Older people may forget to perform an action, such as posting a letter, keeping an appointment or taking medication, but, being aware of their frequent memory lapses, are more likely to use memory aids such as diaries, alarms and other reminders. As with other cognitive capabilities, the degree of decline or impairment in resources to deal with complex decisions is strongly associated with education and experience. Problem solving and decision-making are also influenced by social and political attitudes, cultural background and individual attitudes towards taking risks. Increasing life expectancy has placed a high value on independence and self-reliance, meaning that executive function capabilities are more important for older people than ever before (Huppert 2003).

9.2.6 The psychological feel-good factor

Some attitudes remain largely unchanged from youth – hence the common feeling that what is odd about growing old is that you do not feel any

different (Metz and Underwood, 2005). The most basic life value is the will to live, and the most basic behaviour consists of acts in service of self-preservation. 'Survival scenarios are the sum total of everything needed for a safe, comfortable, and pleasurable existence' (Wolfe and Snyder, 2003). 'There is an increasing emphasis on disciplining the body through virtuous nutrition and physical exercise, together with social engagement' (Metz and Underwood, 2005). 'Most design-oriented research on older consumers tends to focus on older people in isolation, rather than within the context of their extensive kin network with its implications for time use, communication, travel and spending' (Huppert, 2003). In terms of outdoor activities, 'surveys find that walking is by far the predominant activity reported in surveys of older people, half the men in their 60s and 40 per cent of women reporting this' (Metz and Underwood, 2005).

This chapter looks at the application of smart textiles that may enhance the functionality of a multi-purpose, protective 'clothing layering system' for the benefit of older people. It looks at how the appropriate design of smart clothes has the potential to promote independence and wellbeing, and may enable participation in healthy exercise in the everyday lives of the active ageing.

9.3 The clothing layering system

9.3.1 The sports-type layering system

The functionality of the sports type 'layering system' is driven by textile innovation as a basis for the application of emerging smart textile technologies into lightweight, compact and easy-care protective clothing for the ageing community. The system typically comprises a moisture management base-layer, mid insulation layer(s), and a protective outer layer. Textile innovation now embraces the concept of the 'soft shell' that incorporates a hybrid mix of the protective attributes of the outer shell garments with the comfort and insulation of mid layers. In addition, with the introduction of textile-based sensors, there is a need for a close fitting 'skin layer' for men and suitable intimate apparel for women. Key aspects of the maintenance of comfort are effective moisture management and thermal regulation through the application of special fibres and fabric constructions, and the provision of ventilation within the garment(s). In the case of the ageing wearer, elements of personal protection may be incorporated into the system. To function effectively, the garments, and components within the layering system, should benefit from technical and aesthetic design coordination in terms of style, fit, silhouette and movement, as well as suitability and positioning of details and closures (McCann *et al.*, 2009). The layering

system may now have enhanced functionality to help address demands of the ageing body through the incorporation of smart textiles in both clothing and accessories. The design, overall comfort and the usability of the technology interface are key to user acceptability.

9.3.2 Base layer/skin layer

The base layer is normally of knitted construction, with varied structures placed around the body to aid moisture wicking and offer increased support and protection. Older people may be at risk in relation to survival in extreme cold if a high moisture level is absorbed within the garment base layer and the temperature drops. There are obvious advantages in the application of high moisture wicking, quick drying textiles for the onset of incontinence. Microcapsules containing specific additives, such as aroma therapeutic essential oils, may be impregnated into the fibres. The attributes of stretch fibres have revolutionised the technical and aesthetic design and comfort of 'underwear' and intimate apparel, and may be incorporated, in varying percentages, in warp and weft knitted structures, laces and nets, woven constructions and narrow fabrics. The properties of elastomeric and mechanical stretch are of particular relevance to garment design for older figure types. A varied percentage and direction of stretch enhances comfort and fit in providing engineered areas of support or enhanced movement that enables the wearer to put on and take off the garment with greater ease. Stretch also contributes directly to garment fit and to the embedding of textile sensors and wearable electronics to be held in appropriate locations within garments, currently found in close fitting base layer garments and bras for sport and for medical applications.

9.3.3 Mid layer

The mid 'insulation layer' may be varied in thickness, or bulk, to effect its ability to trap 'still air' for heat retention. It may be made up of more than one garment, with examples such as jackets, smocks, gilets, traditional knitwear and felted garments. Typically, the insulation is made up of lightweight man-made down, sliver knit constructions known as fibre pile or fake fur, and increasingly sophisticated developments in knit structure fleece fabrics, primarily in weft knit, and predominantly of polyester fibre. Fleece pile garments may have 'body mapped' engineered knit in varying patterning, depths of pile and finishes, to provide variable protection around the body (McCann *et al.*, 2009). Older people are susceptible to cold and may benefit from adaptations of existing and emerging technologies initially adopted in

performance sportswear, such as heated panels. Mid layer garment design should be compatible, in terms of cut and styling, with that of the base and outer layer garments, to avoid impeding movement.

9.3.4 Soft shell

The 'soft shell' layer incorporates many of the protective elements of outer shell garments, combined with the comfort and insulation of mid layers. Soft-shell fabric technology is normally a laminated assembly of two fabrics with a membrane in the middle. Typically the layers comprises a combination of polyester or nylon woven face fabrics backed by light-weight, to high loft, knit constructions with an inner membrane intended to allow airflow through the fabric but prevent water from penetrating from the outside. These garments are designed to be water repellent rather than waterproof and do not require seam taping. The fabrics are softer and less noisy than more protective 'hard shell' garments and often have a degree of stretch to enhance comfort and fit. As extreme protection is not required on a daily basis, this category of garment, if designed to suit older people's style requirements and figure types, may offer an attractive solution to adaptable and comfortable lightweight protection for everyday use.

9.3.5 Outer layer

The outer layer, or 'shell', provides protection for the clothing microclimate from the ambient conditions. This may be provided by waterproof breathable textiles in a range of variations on woven or knit structure protective textile assemblies with additional properties and finishes, such as abrasion resistance, for more extreme requirements (McCann *et al*., 2009). Outer garments have become increasingly lightweight, fitted and stylish, with enhanced comfort, through moisture management, in hydrophilic or micro porous waterproof 'breathable' membranes with stretch properties. The concept of 'Body Mapping' identifies areas or 'zones' for the placement of textiles in relation to comfort factors such as ease of movement and articulation, predominant posture, moisture management, thermal regulation, impact protection, environmental protection and enhanced visibility. Novel joining methods, such as the heat bonding of seams, zip insertions and laminated panels, have revolutionised appearance and reduced bulk. Heat bonding also contributes to the encapsulation of wearable electronics, as safety and communication devices, with their textile-based switches and controls. To date, such garments have seldom been designed with consideration of the style and usability requirements of older wearers.

9.4 Smart protective textiles for older people

9.4.1 Defining smart textiles

Emerging wearable electronics have the potential to provide additional functionality within the clothing layering system, in monitoring activity, movement and positioning, temperature regulation and subsequently, over time, provide sufficient data to detect behavioural changes. Smart textiles may provide significant new understanding of the effects of ageing and alert the user, by providing informative feedback. Technological advances permit power and signal pathways to be integrated into garments, and accessories to facilitate applications such as heart rate, temperature and respiration sensing, location monitoring, and social and emotional contact. Smart textiles may be defined in three subgroups; 'passive smart', which sense environmental stimuli, 'active smart', which sense and react to the environmental condition or stimuli, and 'very smart', that can sense, react and adapt their behaviour to the circumstances (Van Langenhove *et al.*, 2007). Smart textiles require a sensor, an actuator (for active smart textiles) and a controlling unit (for very smart textiles). 'Passive Smart' textiles, used in clothing applications, may provide attributes such as UV protection, conductivity and embedded optical sensors. 'Active Smart' textiles provide functionality such as shape memory materials, thermo-chromic dyes with chameleonic characteristics, hydrophilic waterproofness, moisture management and phase change properties. Electrically heated textiles are also within the Active Smart category. 'Very Smart' textiles may deal actively with life threatening situations, comprising a unit with cognition, reasoning and activating capacities. Textile-based sensors for monitoring vital signs are in this category (Ajmera *et al.*, 2007). For examples see Table 9.1.

9.4.2 Size and shape

A key design consideration, throughout the garment layering system, is in addressing the changing size and shape of the ageing body with consideration of fit, movement, and the accommodation of predominant postures for both wearing as well as putting on and taking off the garment. Changes in bodily dimensions, including age-related shrinkage in height, should be considered in the design of clothing and accessories. The placement of wearable electronics, with textile-based sensors, for the recording of vital signs and/or positioning and movement, is critical in relation to the size and shape of the body. In the SizeUK National sizing survey, completed in 2004, three-dimensional body image processing was used to capture body measurements to determine the size and shape of a cross-section of the population (www.size.org). Body scan measurements may be stored on a database to

Table 9.1 Examples of applications within the smart clothing layering system.

	Skin layer and intimate apparel	Base layer	Personal protection	Mid layer	Soft shell	Outer hard shell	User interface
Passive Smart – *do not involve any alteration to the environment*	Moisture management. Mechanical stretch. Elastomeric variable stretch. Engineered knit 'body mapping'.	Moisture management. Thermal regulation. Seamfree engineered knit 'body mapping'.	Spacer fabric. Impact protection. Innovative engineered spacer knits, e.g. Baltex (Karl Meyer).	Insulation: knitted fleece, fibre pile, down, etc. UV protection e.g. Solumbria, Coldblack® and Tencel Sun.	Moisture management. Water repellence.	Moisture management. Windproof/ waterproofness/ breathability: coatings and laminates.	YKK easy access, open ended zip.
Active Smart – *have sensors and actuators that tune functionality to the environment*	Micro-encapsulation and antimicrobial additives, e.g. silver. X-Static, SmartSilver, Polygiene.	Micro-encapsulation and antimicrobial additives. Yarn based warming underwear, e.g. WarmX	Memory spacer knits, e.g. Baltex. Silicon coated shock absorbing Deflexion™ (Dow Corning).	Garments with heated panels and controls, e.g. Polartec®Heat® and Fibretronic Heat-wear.	Active smart membranes. Phase change materials (PCMs). Far infrared rays, e.g. Energear (Schoeller)	Phase change. Biomimicry, e.g. Outlast, Schoeller, C-change. Visibility/ reflectivity.	Magnetic snap fastenings.
Very or Ultra Smart or Intelligent – *sense, react and adapt to environmental conditions or stimuli*	Textile-based sensors for vital signs monitoring: heart rate etc., e.g. Santoni seamless knit (Adidas), Shima Seiki whole garment knit (Smartlife)	Scan2Knit for customised DVT support. Far infrared rays to improve blood circulation, e.g. FIR-TEX.	Spacer fabrics with embedded sensors.	Textile-based sensors. Accelerometers for posture, positioning and activity monitoring.	EY Technologies iCon Fibre smell detectors. Soft controls: GPS: positioning and movement. Lighting, LEDs. Power (Solar). Alarms (Recco).	EY Technologies iCon Fibre smell detectors. Soft controls: GPS: positioning and movement. Lighting, LEDs. Power (Solar). Alarms (Recco).	Flexible screens, textile controls, speakers, etc., e.g. Fibretronic ConnectedWear. Watch, e.g. Sony Ericsson Live View, Smartphone.

be retrieved for individual customers to inform the customisation of garments made to measure. In theory, this process may also make it easier for people with disabilities or restricted mobility to purchase clothes that fit (Metz and Underwood, 2005).

9.4.3 Smart protection within the skin layer

This section discusses:

- vital signs monitoring,
- compression garments,
- support hosiery.

Vital signs monitoring

Wearable electronic devices for physiological monitoring have been introduced predominantly in the areas of performance sport and corporate work wear, and in medical applications. Design-led garments have been developed predominantly for young athletic figure types with little consideration for the less predictable figure types and postures, and the relatively restricted movement and agility of older people. Typically, textile-based sensors are either incorporated into seamfree knit garments, such as those using Santoni technology (Adidas) or Shiema Seiki engineered knit (Smartlife); or in more restrictive straps (Zephyr). Heart-rate sensing apparel links wearable technology to the promotion of health and wellness; for example, through the Adidas miCoach programme. Seamfree Santoni knit sports bras, and close fitting vests for men, use textile-based sensors incorporated into the structure of the garments, based on technology initially developed by Textronics. A separate heart rate monitor snaps into a small pocket within the garment and sends heart rate feedback to the miCoach Pacer or Zone. The system is described as a personal training solution, to help motivate the wearer towards reaching their personal fitness goals, combining real-time coaching with an intelligent web application, the miCoach Zone. On entering the wearer's age, the web application calculates the appropriate target training zones. LED lights in the wristband clearly display the wearer's heart rate zone as they exercise, making it possible for the individual wearer to train at an appropriate intensity (http://www.adidas.com/uk/micoach).

SmartLife® Technology's 'softsensor' system is based on knitted sensor structures, integral to the garment's manufacture, and based on a dry interface with no reliance upon gel-based facilitation, forming 'a wide variety of on-body, dry sensor wearables and traditional garments for the monitoring of real time vital health signs, such as ECG, heart rate, EMG, respiration,

tidal flow and other sensory inputs – all to comparable clinical quality standards' (www.smartlifetech.com*)*. It is claimed that the e-textile data integrates seamlessly with wireless, mobile and existing equipment, either in the home, the clinic or in a pocket. In terms of user-interface, the 'textile integration automatically ensures their position is easily located, and the wearer requires little introduction or support instruction for either the set-up or the ongoing and compliance of routine remote monitoring.' Data collected by these washable garments can be transmitted in real time via Bluetooth to a remote computer, PDA, or cell phone.

The Zephyr Bio Harness™ measures critical vital signs (ECG, heart rate, breathing rate, skin temperature) and contextualises the information with the individual's physical activity, using an accelerometer that monitors activity, and posture. Radio interfaces, such as smart phones and tactical radios, transmit the data to those who care and need to make critical decisions based on an individual's physiological status (www.zephyr-technology.com). Although the garments and straps described include textiles to facilitate the monitoring of vital sign information, a physical device is still required for data transmission and processing. Advances in electronic engineering allow these devices and processor to become much smaller and more ergonomic (W. P. H. Burns, 2010, personal communication).

Compression garments

Maintaining good blood circulation in the body plays a major role in maintaining good health as the means by which oxygen and nutrients are carried around the body. Improving poor circulation is central to helping stave off a manner of debilitating disorders, from diabetes to heart disease to varicose veins or the inability to think clearly. Compression garments can assist in enhancing circulation and are commonly recommended for anyone where this is lacking, including athletes, surgical patients, oedema patients and anyone with a sedentary lifestyle. An effective means of treating oedema is the use of high-quality compression hosiery that provides compression support at the ankles, with the compression gradually decreasing up the leg. This improves venous return in the leg and helps to lessens the pooling of fluid in lower extremities. Compression clothing is designed to improve and accelerate healing, promote improvements in blood flow, and reduce the risk of soreness and injury from strenuous exercise. Variable stretch engineered knitted textiles may offer targeted support in maintaining muscle alignment and a reduction in the loss of energy in athletic performance. Additional reinforced taping, outlining and supporting muscle groups, contributes to the aesthetic appearance of the garment. In swimwear and in other athletic sports applications (e.g. Adidas), it is claimed that

bonded seaming and appliqué constructions offer support and muscle control, to promote proprioception.

Support hosiery

Body scanning directly informs the design and fit of customised compression hosiery. The William Lee Innovation Centre (WLIC), in Manchester, has created a system called Scan2Knit based on Shima Seiki technology, in a project led by Dr Tilak Dias in the research of three-dimensionally shaped and seamless fibre assemblies for technical textiles and apparel applications. Bespoke medical garments have been developed for people who have developed severe ulcers through age, infection or injury, to improve the effectiveness of compression bands that apply pressure, which forces lymphatic fluid towards a functioning lymph node. The specialised computer-assisted manufacturing process involves scanning the leg and foot with a 3D limb scanner, to construct a 3D model from the scans, with the information then transmitted to a dedicated computerised flat-bed knitting machine. A bespoke stocking is then accurately engineered to apply a prescribed 3D pressure profile to the leg. The Scan2Knit technology has also been adapted for the manufacture of compression sleeves for the treatment of lymph oedema. The WLIC has collaborated with an industrial partner, Advanced Therapeutic Materials Ltd, to commercialise the innovative Scan2Knit technology. A two-year patient study using this has taken place at Withington Hospital in Manchester, commencing in September 2006 (Dias *et al.*, 2011).

A German company, WarmX, produces a range of ergonomically designed, electrically-heated clothing for outdoor sport activities, as well as for the professional working environment of both men and women. It is claimed that sufferers from muscular tension and certain back or renal problems benefit from the soothing and analgesic effect provided by heat applied directly to the skin. WarmX heatable, one piece, seamless, flat-knitted tights are wireless, with warming zones placed directly against the skin, at the feet. The tights are constructed from a blend of 49% cotton, 9% elastane and 40% nylon, with 2% pure silver plated onto polyamide threads woven into the underwear, with a greater percentage in the foot area, to warm up directly on the skin. As well as conductivity to enable heating, the silver combats bacterial increase and odours. A mini power controller is situated in a small pocket in the upper left side front of the tights or, alternatively, an extension power controller may be worn in a trouser pocket. The tights, and a range of other heated garments, are powered by a Li-ion battery with a guaranteed retention of 80% maximum capacity after 500 recharge cycles. The power controller and charger are offered separately (http://www.warmx.de).

9.4.4 Smart protection within the base layer

This section discusses:

- far infrared rays technology,
- antimicrobial additives,
- phase change materials.

Far infrared rays technology

The company FIR-TEX (Far Infrared Rays TEXtile) claim that their technology captures thermal radiations emitted by body heat, then, reacting like a 'reactive mirror', uses thermal Far Infrared rays to send energy back into the cells and tissues of the body. The Far Infrared frequency is said to deeply penetrate the skin layer to resonate with the water and organic molecules of the body. As the FIRs interact, the water molecules are set into a rotation state, resulting in energy transfer as the thermal reaction increases tissue temperature. The human body is said to react to this phenomenon by dilating blood vessels, resulting in improved blood circulation with more oxygenized blood reaching muscles and tissues. This technology is claimed to reduce abnormally-shaped blood cells and also to enable the separation of blood cells to become less 'sticky' (from sugar/protein). This is intended to optimise the delivery of oxygen and the elimination of waste gases from the entire organism that, if achieved, instantly improves the aerobic energy system and puts less strain on the heart. Evidence from tests claims that FIR-TEX technology can improve the wearer's balance, mobility and global performance due to improved blood circulation (Wilson, 2010).

Antimicrobial additives

Antimicrobial silver additives have been introduced to provide protection from hospital-acquired infections, with evidence that clothing is a key carrier (Anon, 2010). A variety of textile treatments contain silver, which contributes to eliminating odour-causing bacteria and athlete's foot fungus. X-Static has a layer of pure silver, permanently bound to the surface of a fibre, containing about 15% pure silver, manufactured to retain traditional textile and tactile characteristics. Whilst X-Static has anti-microbial properties, it is suited to provide additional features such as heat transfer and anti-static properties due to silver having the highest electrical conductivity rating of any element. With its conductive properties, this fibre system is also claimed to have many health and circulatory benefits.

Another antimicrobial product, SmartSilver, has been bound into the material of a range of hospital clothing. It is made of 75% recycled polyester

and 25% cotton, called ‘Do NO Harm’, and was launched in the US by NanoHorizons.

Sweden’s Polygiene ionic silver technology (www.polygiene.com) also claims to have permanent resistance to odour-causing micro-organisms, with 100%-recycled silver ions that continuously migrate to the textile surface where they effectively suppress microbial growth.

Phase change materials

Temperature-regulating phase change materials (PCMs) were first introduced by Outlast Technologies Inc. as paraffin wax ‘Thermocules’, encapsulated into acrylic fibre and subsequently into viscose. This technology absorbs, stores and releases body heat, adopting latent heat principles – the heat released or absorbed by a chemical substance or a thermodynamic system during a change of state or phase transition. As the body heats up, the wax stored in the phase change molecules turns to liquid and stores the heat. As the body cools down, the wax solidifies and, in so doing, releases the stored heat back to the body. Products must be worn next to the skin for ultimate function. Recent examples include T-shirts and long trousers, designed to wear under maintenance workers’ uniforms, in a fabric made up of 48% Outlast, 48% viscose and 4% spandex (Anon, 2010). A new generation of Outlast’s ‘Adaptive Comfort’ technology consists of bicomponent fibres with a polyester sheath and a core injected with the PCM. Initially available as a staple fibre but with a filament version to follow, it is claimed that this fibre retains all the characteristics of conventional polyester, such as low moisture absorption, moisture transport, good wrinkle resistance and durability, but with the ability to regulate heat (Swantko, 2002).

9.4.5 Protection within the mid layer

This section discusses:

- sun protection and
- heated garments.

Sun protection

With ageing, the skin’s layers lose the ability to retain fluids with a loss of some of the fatty deposits under the skin and a loss of elasticity, resulting in the skin becoming wrinkled, dry and easily bruised. To minimize these effects, direct sunlight should be avoided. The sun’s damaging UV rays promote skin cancer, with many cases of melanoma diagnosed each year and many people dying from this disease. For elders, 80% of UV

damage has occurred in childhood and adolescence, when people were not aware of the risk of exposure. The Ultraviolet Protection Factor (UPF) measures the amount of UV radiation that penetrates a fabric and reaches the skin. For example, a white T-shirt provides only moderate protection from sunburn, with an average UPF of 7, while a long-sleeved dark denim shirt offers an estimated UPF of 1700, which amounts to a complete sun block. If one can see through a fabric, then UV radiation can penetrate it and the skin. In general, clothing made of tightly-woven fabric offers best protection, with darker fabrics more effective than lighter colours. For example, the UPF of a green cotton T-shirt is 10 versus 7 for white cotton, and a thicker fabric such as velvet, in black, blue or dark green has an approximate UPF of 50 (http://www.skincancer.org/sun-protective-clothing.html). Moisture wicking fabric constructions may perform badly in the sun and lose up to 50% UV protection when they become damp or stretched. While ‘a wet t-shirt on a swimmer provides at best an SPF [sun protection factor] of 3; dry, the shirt offers on average a factor of 7’ (Brody, 2006).

To prevent new problems for older people, garments should be made of tightly woven fabric, with fine fibres in dark colours, in long sleeved and long trouser styles, with a loose fit to aid cooling. For example, Sun Precautions (USA), has developed Solumbra, a tightly woven, lightweight, cotton-soft and nylon-based material with an SPF of 30, which, even when wet, claims to block out 97% of harmful UVA rays (UV type A) and the UVB rays that cause sunburn (Perman, 2004). Lenzing’s Tencel fibre is relatively eco-friendly; it is based on man-made cellulosic fibre manufactured from wood pulp, and is claimed to be 100% bio-degradable. For sporting activities, ‘Tencel Sun’ has permanent pigment integration coming from minerals, with protection due to moisture absorption that swells the fibres, claiming to provide long-term protection from solar radiation, with an SPF of 110 (www.lenzing.com).

Coldblack® technology, developed by Schoeller Textiles, is said to reduce the heating up of textiles exposed to sunlight and offer protection against UV rays, through a combination of absorption and reflection (www.coldblack.ch). Schoeller acknowledges that light coloured textiles reflect both visible and invisible rays of sunlight with both light and heat radiated back. In contrast, dark fabrics absorb both types of radiation and therefore absorb heat. Coldblack® claims to reduce the absorption of heat rays, particularly in darker colours, and guarantees a minimum UPF of 30 when applied to any textile in any colour without affecting the look or feel of the product. The UPF value can vary depending on the structure and thickness of the material with tight structures recommended. Normally black textiles without coldblack® absorb up to 90% of the heat rays, and heat up accordingly, while textiles with coldblack® are claimed to reflect up to 80% of the heat rays and therefore stay noticeably cooler (http://www.coldblack.ch).

Heated garments

Fabric-based heating elements are now being embedded into clothing, gloves and other accessories. The fleece fabric producer Polartec has introduced Polartec® Heat® panels that can offer instant warmth in a fitted garment that can either stand alone or work within a layering system. Using a lithium-ion battery pack, the conductive heat panels are incorporated into the garments to provide warmth beyond that which the wearer's body heat can generate. A wireless remote control enables the wearer to change the heat levels easily. The core garments, in male and female fit, are in lightweight textiles but the detachable Polartec® Heat® components, that include the heat panel, the battery pack, and the remote control, are not washable (www.polartec.com/warmth/polartec-heat/). A comparable product, the Fibretronic HEATwear system, is co-branded with Ripcurl in a padded gilet. This fabric heating panel is powered by a rechargeable Li-ion battery weighing 160 grams, with four power settings available and providing between 3 to 6 hours of continuous heat. An LED control switch is integrated in the chest of the garment to enable the wearer to understand the operation of the heat settings (http://fibretronic.com).

9.4.6 Protection within the soft shell layer

This section discusses:

- novel manufacturing techniques and
- textiles to enhance wellbeing.

Novel manufacturing techniques

Hybrid 'soft shell' garments have a relatively soft and quiet handle and provide lightweight, stretch, water repellent and breathable protection that, with appropriate design, may offer an ideal product for protective outerwear for older people. Heat-bonded seaming contributes to clean design lines, with the potential for encapsulated, textile-based electronics and soft switches as the user interface for wearable devices. Garment design is becoming increasingly sophisticated, with typical features such as an outer face in a water repellent stretch nylon weave laminated to a soft inner fleece fabric having a medium length pile and a waffle structure, for improved breathability. Typically these 'sandwich' constructions, used in protective areas, have an inner membrane while side panels may be un-laminated for comfort and freedom of movement. Enhanced protection may be provided in shoulder sections with an additional layer of laminated, abrasion-resistant material. The design may have additional protective features, such as reflectors (Recco) on the arms to provide enhanced visibility and to help

locate people in trouble by bouncing back high frequency signals emanating from search teams.

Textiles to enhance wellbeing

'Energear' is the name given to a soft shell fabric innovation, promoted by the innovative Swiss textile producer, Schoeller Textile, as a further example of a textile 'based on the ancient knowledge about the capacity of certain minerals to radiate Far Infrared Rays (FIRs). The material matrix has been formulated to ensure that the energy radiated by the body is reflected back to the wearer, with the additional energy recovered positively affecting performance capacity and wellbeing.' The reflection of the FIRs claims to promote blood circulation and increases oxygen levels in the blood, with positive effects on the body in performance enhancement, prevention of premature fatigue, improved regeneration, faster warm-up phase, increased concentration capacity and general wellbeing. In tests on 'people in an active, aerobic phase wearing energear™, a lower pulse rate and an increase of air intake could be observed. Improved performance capacity and lower acidity due to the increased air intake were recorded.' A range of Energear soft-shell fabric qualities offer wind and weather protection for leg wear, and jackets for activities such as trekking and urban wear (www.schoeller-textiles.com/en/technologies/energear.html).

9.4.7 Protection within the outer layer

This section discusses:

- biomimicry and
- sensory protection.

Biomimicry

It is no longer necessary for older people to wear heavy, stiff and noisy waterproof garments. Innovations in waterproof/breathable and windproof protection, adopted in sportswear, offer an attractive alternative to relatively heavy traditional outerwear, with multi-functional, exceptionally lightweight fabrics suitable for recreation, travel and urban wear, having low packing volume. For example, 'Schoeller-aeroshell' and 'Schoeller-spirit' fabrics are manufactured as two-way stretch, semi-transparent, 3D honeycomb constructions that incorporate branded c_change technology. C_change is a phase change textile based on bio-mimicry related to a study of fir cones, which expand and contract in humid or dry conditions to create a balance of breathability and waterproofness. The uneven surface of the lotus leaf has also been mimicked, in nano scale, in Schoeller's self-cleaning

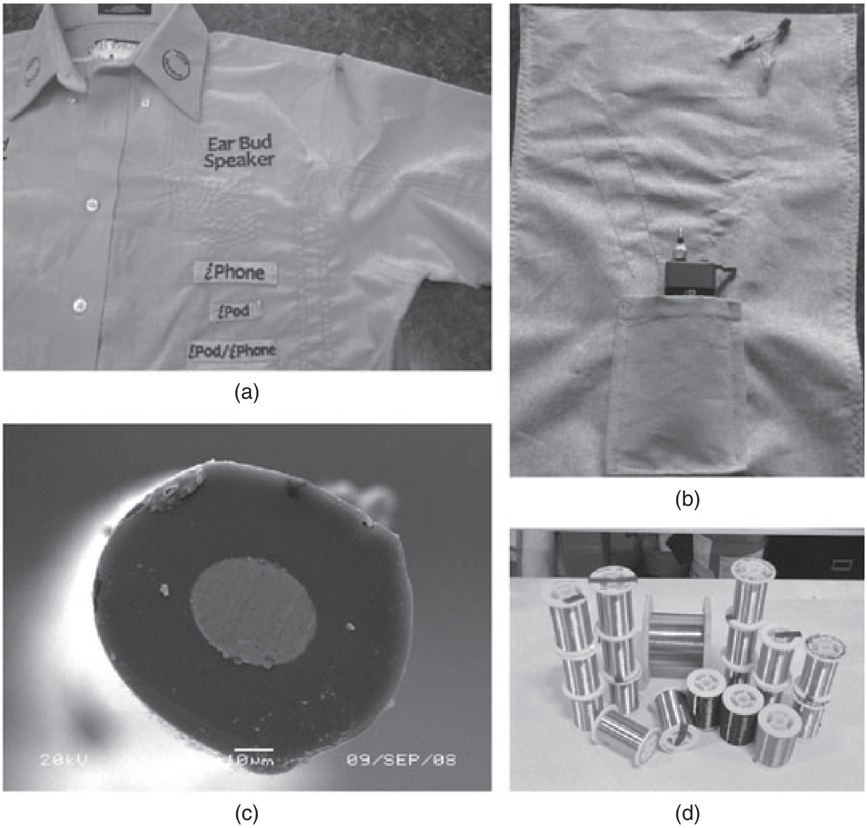
NanoSphere finish that has moisture repellency and stain proof attributes. Additional functionality may be added to outerlayer garments from treatments such as tick and mosquito protection (INZECTIC™) and, as already mentioned, heat and UV protection (coldblack®).

Sensory protection

Smart fibres that can sense dangerous smells can be designed and incorporated into garments giving the users an early warning of dangerous environments. R. Perera, of EY Technologies, USA (2010, personal communication), states that the biggest hurdle has been the lack of textile-grade insulated micro conductors, but that there is now the potential for nano particles to be introduced as sensory protection for smell detection in outer layer garments. Intelligent fibres, acting as electro chemical captors, can be formulated to detect harmful gases such as carbon monoxide, gasoline, household gas, fumes and bio threat material. EY Technologies have introduced insulated 'iCon-75' fibre, a novel commercial method of producing fine, insulated, highly conductive filament yarns that are flexible and can be soldered for incorporation into fabrics for use as wearable electronic circuitry. These fibres can also be integrated into garments for entertainment and communication applications, with a town walking global positioning system (GPS) envisaged for people having visual disabilities (see Fig. 9.1).

iCon-75 fibre is a textile-grade fibre containing an insulated conductive core that has been specially designed for sensor applications. For example, to achieve the maximum surface area (current), round fibres are not preferred in sensor applications. However, for textile processing easiness, round-shape fibres are always preferred. Additionally, the current generated on the fibre surface must be transferred to the metallic core through the insulating sheath. Thus the iCon fibre must be designed with conductive channels that connect the surface to the conductive core. The round fibre is extruded with a core (60%) of a lower-melting point metal within a textile grade sheath of a higher melting point polymer. The fibre is of 25–75 microns (human hair is 110 microns), and is comparable to 5 denier PET. The filaments are fine, yet strong and flexible, with fibre-like qualities and may be produced with multiple polymer options. They can be woven, knitted, or braided, and finished, either visibly or invisibly, on standard equipment, leading to intelligent, wearable products with improved conformability, flexibility and comfort, and may be machine washed, dried and ironed. The filaments are produced in a variety of colours in 25+ microns on spools of 5000 metres, in blends of nylon, wool and PET, with either a single conductor or multi conductors.

Properly chosen nano-powder chemistry, applied on EY Technologies iCon fibre as a coating, can react with dangerous fumes, generating



9.1 EY Technologies smart shirt prototype (a and b) with iCon fibre (c and d). (Courtesy of R. Perera, EY Technologies.)

electricity by an electrochemical ion exchange mechanism. This surface electricity can be transferred to the conducting metallic core which can then activate an audible or visible signal built into the garment. In order for the system to work, the incoming fumes should create an electrical potential between two wires connected through the alarm system. One way to achieve this potential difference is to have two conductive fibres having two different surface chemistries. When a toxic gas comes in contact with the surface of each fibre, they will produce two differing potentials and the system will act as a battery. If the two fibres (now acting as electrodes) are connected through an alarm system, this will result in a current flow through the system, triggering the alarm (current flows from the higher potential to the lower potential). It is not even necessary to have two surface chemistries. The same results can be obtained using one chemistry, by changing the concentration of active particles applied on each fibre. In such a situation,

one fibre will have higher potential than the other. These fibres and fabrics can also be used as strain gauge sensors, temperature sensors and as structural integrity monitors (R. Perera, 2010, personal communication).

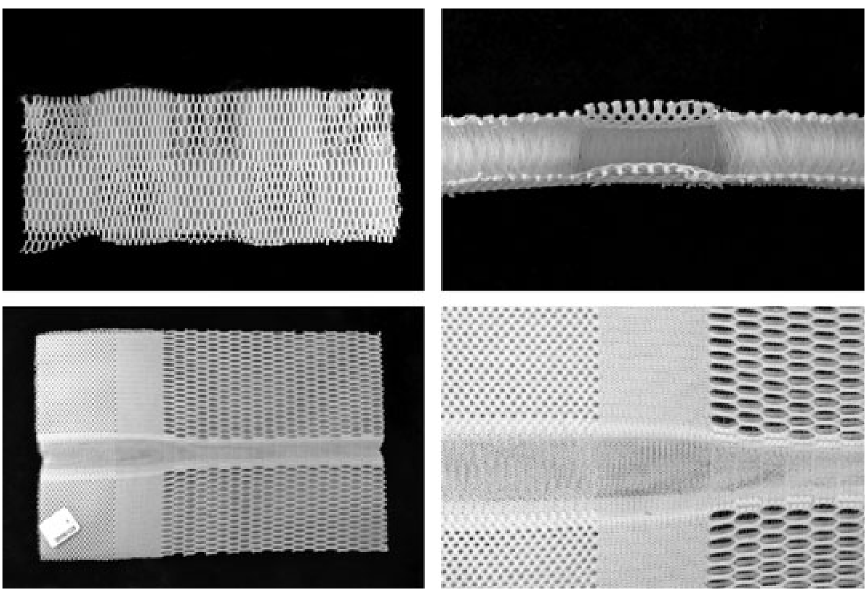
9.4.8 Smart body protection

The psychological 'feel-good factor' is directly related to the reliability of, or the perception of the reliability of, the garment system. Designers must give consideration to vulnerable areas of the body in anticipating injurious hazards and commonly occurring accidents – in particular, falls. Positioning and movement may be tracked in terms of detecting falls but also, from a more positive view point, in monitoring progress in keeping fit or in exercise for rehabilitation. The incorporation of stretch sensors in stockings, knitted sleeves, or other garments, may be used to track the wearer in terms of angle of movement for training or rehabilitation and/or alert the person regarding the need for movement to reduce interstitial fluid build-up and reduce blood stasis in lower limbs. Smart textile structures may provide lightweight personal impact protection for older people. Researchers have found that among walking elderly adults, the risk of hip fracture can be reduced by 80% if a hip protector is worn at the time of a fall. (Sheil, 2008). There are on-going developments in inherently flexible phase change materials that harden on impact and then revert to a flexible state once the impact has passed, which have the potential to offer protection to older people.

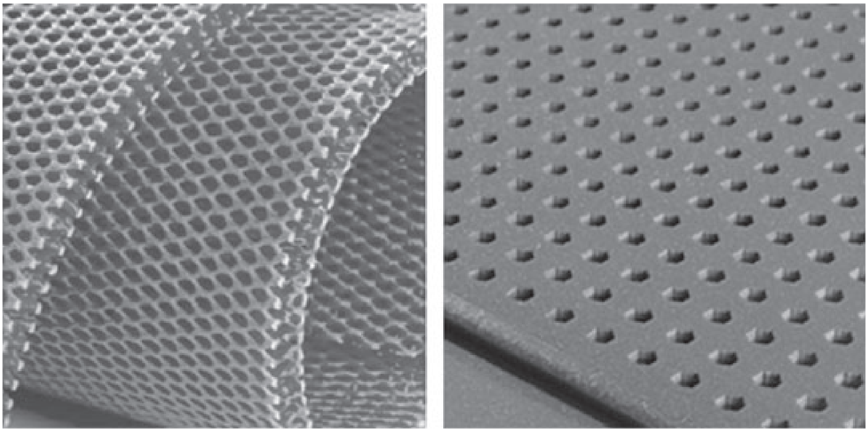
Baltex is a specialist knitter, leading innovation in spacer textiles in the UK. Their 3D knitted spacer fabrics are primarily produced on double needle bar warp-knitting machines in thicknesses that vary from 3 mm to 20 mm, using both warp-knit and weft-knit technologies. The warp knitted structures consist of two separately produced layers that are joined back to back, may be produced from different materials, and can have completely different structures. The yarns that join the two face fabrics can either closely join the layers or space them apart, with this 3D space as the special feature of such structures. Spacers can also be knitted on weft machines, in 3D structures on a circular machine, or on electronically controlled flat machines. In providing added dimension, spacer fabrics are being widely used as for the replacement of foam, cushioning and neoprene products. With the possibility of knitting different fibres on different faces, in different thicknesses and surface designs, many properties can be achieved for a range of end uses. Principal advantages of spacer textiles include breathability, insulation, compression strength, durability and pressure redistribution, with the potential for recycling. Yarn selection can vary from natural to synthetic fibres, and microfibres, to include polyester, polyamide, Kevlar and Nomex (Baltex, 2010, personal communication).

Spacer fabrics may be produced in a range of weights and depths, suitable for plasters and bandages to mattresses, and may be heat moulded for applications including footwear soles, compression bandages, orthotics and body armour. Stretch, and two-way stretch, may be added for use in orthopaedic bandages and slings. One product is described as a 'memory spacer' that, when shaped, retains its curved form, offering enhanced comfort, fit and protection of the body in healthcare and military applications, in addressing the shape of arms, knees, elbows, breasts, etc. Rib spacer constructions provide relative rigidity with regular open channels to enhance airflow within the textile assemblies. Some qualities may be produced in a range of different colours with added functionality such as softeners, fire retardancy, infrared reflective treatment, and silicon and fluorocarbon finishes. Branded fibres and treatments may be added, such as Coolmax polyester for enhanced wicking and Polygiene with antibacterial properties. Further innovative engineering of spacer knit constructions has been possible through the development of the knitting techniques, in collaboration with the machinery producer, Karl Meyer (see Fig. 9.2). A body mapping effect may be knitted into the fabric repeat through the variegated engineered patterning of stitch structures and the varied depth of the spacer monofilament areas.

The chemical producer, Dow Corning, has introduced the brand name 'Deflexion', which embraces two smart textile technologies for extreme



9.2 Examples of engineered spacer fabrics by Karl Meyer. (Photographs by David Bryson.)



(a) (b)

9.3 Deflexion from Dow Corning. (a) S-range and (b) TP-range impact protection textiles (http://www.dowcorning.com/content/deflexion/deflexionmaterials/).

protection (see Fig. 9.3). The S-range features the application of silicone on open spacer knit constructions that remain relatively soft and flexible under normal conditions, but can absorb and disperse the shock of impact. 'Unlike bulky hard-armour component systems, Deflexion™ protective textiles can be incorporated directly into garments and accessories to shield the wearer against high energy impacts.' The fabric may be multi-layered for increased protection and may be bonded to other textiles using silicone adhesives. Prepared protective parts, cut to ergonomic shapes, may be fully integrated into a garment or inserted into a pouch or cavity. This fabric technology has been tried and tested in extreme sports clothing, for example, in motor bike clothing, by Rukka, Finland and is to be launched in sailing wear as Henri Lloyd's Shockwave range (Rogers, 2010).

Dow Corning's TP-range combines the properties of silicones with thermoplastics and is available as flat sheets, either with holes for maximised airflow, or as a solid sheet (see Fig. 9.3). The versatility of the technology enables the development of different surface effects, and, in cutting the material to any desired shape, provides an appropriate design and feel for targeted applications. In two thicknesses (3 mm and 8 mm), this material offers varied levels of protection and is relatively thinner and lighter than other protective systems and will sustain performance even at low temperatures. This product has end-uses in body armour for sports, in sport accessories, and as protection for sensitive equipment and electronics such as laptop computers, cell phones, cameras, footwear, and luggage. It also has applications in personal protective equipment with the potential for electronic devices, such as impact measurement or accelerometers, to be

integrated with the material using a compression over-moulding process. Dow Corning has recognised that clear point-of-sale material and instruction manuals are required to aid designers in the application and promotion of both these technologies (http://www.dowcorning.com/content/deflexion/deflexionmaterials).

9.5 Usability of the technology interface

9.5.1 Older people's familiarity with technology

Many studies have revealed that today's older people have become competent users of high-technology products where they perceive that those products deliver something of value to them (Metz and Underwood, 2005). The mobile phone has enabled older people to maintain communications with family and friends, and even to text grandchildren. Improvements in computer interfaces have enabled older people to produce letters with corrections to typing errors. Older people are capable but slower, and those over 50 are the fastest growing group of internet users in the UK; as a group they spend more time on line than any other age group of the population. However, researchers have identified a number of characteristics elicited from usability tests with ageing users of various types of technological equipment. They identified that older people have longer response times, difficulty in collecting a lot of information in a short time, excessive responses to voice messages, repetition of errors, difficulty in noticing changes on a screen and, generally, have a lack of initiative. They noted a better response to items that are easily identified as interactive with, for example, large buttons (Harada and Akatsu 2003). Customising the product to a user's needs by modifying its characteristics, may, for example, involve increasing the font size of visual displays. At present, customisation is usually done by the users. In future, information held on a smart card inserted could effect the customisation automatically (Metz and Underwood, 2005).

9.5.2 Sensory design considerations

Sensory design considerations, in terms of materials selection in garment features and trims, should take account of touch or handle, in terms of dexterity and grip, protection for the eyes, and the avoidance of impeding hearing, taste, and olfactory capabilities. Textile and other surfaces should address the diminished tactile sensitivity of elderly wearers, with changes in texture used for both tactile pleasure as well as for practical end-use and safety (Wolf and Snyder, 2003). Textile switches and touch sensitive displays may aid dexterity, as alternatives to control buttons that may not be further reduced in scale on wearable devices. The design of fastenings

and packaging should take account of a loss of muscle power and, where possible and appropriate, products should be adjustable. Tasks should be achievable using one hand rather than two, to allow for strength variation between the hands, and to allow for balance support while undertaking the task (Huppert, 2003).

Sports gloves have been developed that feature textile-based joystick controllers incorporated in the back of the hand (e.g. Fibretronic's five-function controller for the internationally recognised sports brand, O'Neill). These battery-powered gloves activate heating technologies such as copper wires, nichrome wires, metal 'mesh' systems and carbon fibres. The joystick controller connects to a wireless transmitter located in a waterproof pocket in the cuff of the glove. The transmitter sends the joystick commands to the wearable device, such as an iPod, via a wireless receiver unit which connects to the iPod through the dock connector port. In addition, gloves may be designed with ergonomically placed treatments that enhance grip and dexterity. The Ambit iPhone Gloves, by Outdoor Research, are designed to enable the wearer to answer a call on a touchscreen phone without exposing their hands to cold weather. Patented technology, called TouchTec™, made by Broleco Inc., allows the screen to sense the touch of leather, enabling the use of a touchscreen with gloves on (Regenold, 2011) . Heated clothing for extremities, for hands and feet, would be beneficial for the elderly as well as sufferers of Reynaud's syndrome and other disorders.

Fibretronic is promoting flexibility of a choice of wearable electronic devices for the customer to use within a garment within their standardised 'Connected-wear system.' The system has two parts: a soft keypad or joystick, which is integrated into the garment, and a controller module which connects the garment to a range of personal electronics such as a mobile phone or a music player. Apparel manufacturers can integrate Fibretronic's controls into a wide range of garments to be compatible with selected electronic modules that may be transferred between Connected-wear enabled garments with easy attachment and removal (http://fibretronic.com/connectedwear). This allows a mix and match of modules, and the facility to update the system with additional functions as products are developed. Fibretronic is proactive in looking at the design requirements of the rapidly growing ageing market, who seem reassured by garments that have technologies that may be upgraded.

In terms of putting on and taking off garments, 'choosing the right fastening for a piece of clothing could significantly alter the effectiveness of the item as a whole' and 'getting it right could be a matter of life and death', states Eric Sitbon, founder of Systemmag, Paris. Sitbon (2010) has developed an alternative to traditional closures based on several magnetic fastening systems used to close and adjust clothing. Magnets, made of magnetised ceramic, can have the strength of the fastening adapted to suit the end-use.

The magnet closures are silent and the fibres do not get caught up and damaged, as with hook and loop fastenings. The magnets open instantly, are adjustable (for example, to tighten or loosen collars and cuffs), are waterproof and work well in cold conditions. Applications include clothing and footwear, wrist supports and watches. Clothing products using the system may be machine washed.

In terms of hearing, audible signals should be adjustable where possible, so that both volume and tone can be altered to suit the user. A combination of audio and visual signals increases the chance that messages will be received. Lower frequency sounds should be used to convey important messages. Fibretronic has launched a Bluetooth enabled module that incorporates a speaker, microphone, call answer/hang-up button and speaker volume controls, with a mini USB port for battery charging. The module, designed to be waterproof, may be attached to a garment using Velcro, allowing the wearer to take calls without removing their mobile phone handset from the safety of a pocket. The embedded speaker allows the user to listen to music stored on their mobile phone if so desired.

Changes in visual acuity call for special consideration in choosing an appropriate font, font size, and type and adequate word and line spacing, as well as appropriate surfaces, colours, degree of glare, back lighting, angle of light, etc. Electronic arrays to enhance visibility should be designed with displays that are simple, uncluttered and concise in prioritising important information. Clear graphic symbols should be used as an adjunct to words where possible. Surfaces should be non-reflective, and brightness and colour contrast high. Blue–violet–green combinations should be avoided. Product designers whose work includes design of instrumentation should likewise take these visual changes into account in designing gauges and controls.

9.5.3 Design implications for cognitive capabilities

Designs with the rapid presentation of information where quick decisions are required should be avoided, as older adults process information more slowly than younger adults. Competing inputs, from the same or different senses, increase difficulty in switching attention to monitor multiple sources of information. The users' knowledge should be taken into consideration when deciding what information is to be displayed and how it is to be displayed. A user looking at their current heart rate simply sees numbers. This information is useful only if the user knows what is a good or bad heart rate for their age. However, that user may prefer this information in the form of two colours, red and green; red meaning an unhealthy heart rate and green meaning a safe and healthy heart rate. By using this method, the cognitive load placed on the user is reduced. The use of a glanceable display further reduces this cognitive load. Progress in a task can be represented

in a glanceable way with the use of cultural metaphors. A user completing a walking activity can be shown a screen with textual information complimented with a flower metaphor. The more walking the user does, the more petals will appear on the flower. When the flower is full of petals, then the activity is also complete (Burns *et al.*, 2010; Consolvo *et al.*, 2008).

9.5.4 Powering the devices

Wearable technology within the garment layering system demands power for voice and data communication, health monitoring, emergency, and surveillance functions, as well as infotainment – all rely on wireless protocols and services. Portable electronic devices, such as mobile phones, cameras and GPS, need a wireless, mobile, and sustainable energy supply in order to overcome the problem of batteries running out of power when urgently needed. Solar panels are an environmentally safe way of powering or charging devices while outdoors.

Photovoltaics, as thin film solar cells and panels, may be integrated into jackets, coats, backpacks and accessories. The production process uses thin film deposition where thin layers of silicon are deposited onto flexible substrates, such as polyethylene terephthalate (PET), without compromising the structure due to the silicon layers being only micrometers thick.

Maier Sports, working in conjunction with partners from the 'Solartex' project, developed a prototype ski jacket in 2006 whereby flexible solar cells could generate up to 2.5 watts of power in optimum sun conditions, with photovoltaic elements positioned in ergonomically sound exposed areas such as the shoulders and the back. Ultra-thin, washable micro-cables, sewn into the material, directed the electrical current to a universal point, where a variety of devices or batteries could be charged. Poppers were used to connect the photovoltaic elements to the cables. From a user perspective, a photovoltaic system should be easy to use, comfortable and reliable, offer a universal socket for different charging adapters and devices, and deliver energy at an affordable price. For older users, this demands parts that should be attractive, integrate well with garment design, and be relatively lightweight, washable and maintenance free.

9.5.5 Design to promote safety and security

When engaging in knowledge elicitation of older peoples' design requirements, the issues around safety and perceived danger do inhibit autonomy, independence and a sense of adventure. Individuals, as well as groups, fear the risk of getting lost, being attacked or falling over. Continuing advances in microelectronics create opportunities for improved assistive technology devices. Some applications related to personal safety and security include

the daily management of the home; for example, in controlling access, in terms of who is entitled to enter, and the ability to summon help and/or acquire other services such as location and route finding. Tracking and positioning devices, such as radio-frequency identification (RFID) and GPS, may be used to monitor activity, movement and posture in sports training and in practice. These devices may also be used, with ethical issues addressed, to track those who may be at risk. Geofencing, the ability to set an invisible GPS fence around a predefined area, has been used to monitor and help persons suffering with Alzheimer's disease (Doughty and Dunk, 2009).

9.6 Conclusion

Smart textiles, in appropriately designed applications, have the potential to provide a range of protective attributes in clothing applications that may enhance the autonomy, independence and wellbeing of older people in their everyday lives. To date, many of the developments in textile-based wearable devices have focused on medical end use, with little concern for design aesthetics. Research findings inform us that the motivation for older people engaging in healthy exercise will be increased if, at the same time, the activity provides joint or individual pleasurable experiences, an enjoyment of nature, a sense of adventure, education and entertainment, as well as increased fitness and the prevention of ill-health rather than enforced rehabilitation (Bieker, 2010). In order to encourage the uptake of clothing with emerging technologies with a view to improving the quality of life of older people, the design and functionality of wearable technology should be attractive and fit for purpose, as well as easily understood, easy to use, and easy to service.

This demands the design of smart textile-based products that are attractive and pleasurable to wear by virtue of an appropriate blend of form and function, embracing aspects of size, shape, proportion and fit, balanced with appropriate aesthetic style considerations. A key factor in the adoption of smart textiles and wearable electronics, in combination with the overall clothing comfort and appearance, is the design and usability of the technology user interface. Designers and technologists must therefore work with older participants, their peers, family and carers, to capture and understand their real user-needs and aspirations. It is also important to note that reasonable physical demands can play a positive part in maintaining most older people's physical activity, which in turn reduces physical decline. 'Designs which largely avoid physical demands, such as voice-activation, are valuable for those with severe physical impairment, but may be a disservice to the average older person' (Huppert, 2003).

This chapter has introduced a breadth of emerging technologies, described in plain language, to support a design-led, cross-disciplinary approach in the

selection of smart textiles and wearable technologies for protective clothing applications for older people. It has looked at the functionality of a sport-type clothing layering system and a breadth of smart textile technologies and garment manufacturing techniques emerging within the performance sport and corporate wear sectors, that have the potential to be adopted and adapted to suit the requirements of older people. The author recognises that the hybrid product area of smart clothes and wearable technologies, with particular consideration of the health and wellness of older people, requires a new shared language to inform effective communication within cross-disciplinary product development teams that, ideally, will begin to adopt a co-design approach with older participants and all relevant stakeholders.

9.7 Sources of further information and advice

- Coldblack, Schoeller – http://www.coldblack.ch.
- Connectedwear by Fibretronic – http://fibretronic.com/connectedwear.
- FIR-TEX – www.fir-tex.com.
- Lenzing – www.lenzing.com.
- MiCoach – http://www.adidas.com/uk/micoach.
- Outlast – http://www.outlast.com.
- Polartec – http://www.polartec.com.
- Polygiene technology – www.polygiene.com.
- Size UK – http://www.size.org.
- Sizemic – http://www.sizemic.eu.
- Smartlife – www.smartlifetech.com.
- Warmx – http://www.warmx.de.
- Zephyr Technology – www.zephyr-technology.com.
- www.myseniorhealthcare.com.

9.8 References

Ajmera, N., Priya Dash, S., Ram Meena, C. (2007) *Smart Textile*. [URI http://www.fibre2fashion.com/industry-article/4/335/smart-textile4.asp, accessed December 28th 2010.]

Anon (2010) Performance textiles are fit for work, field work. World Sports Activewear: *Performance and Sports Materials*, 16(5): 14–15.

Bieker, C. (2010) *ISPO Best Ager market research*. Presentation. [URI http://media.nmm.de/47/ispo10_bestager_presentation_eng_24372647.pdf accessed May 16th 2011.]

Brody, J.E. (2006) Do your skin a favour: protect it in summer. *The New York Times*. [http://www.sunprecautions.com/article/nyt accessed May 16th 2011.]

Burns W.P., Nugent C.D., McCullagh, P.J. and Zheng, Z. (2010). The design and evaluation of an activity monitor for persons with chronic heart failure', *7th*

International Conference on Wearable Micro and Nano Technologies for Personalised Health, Berlin, Germany.

Consolvo, S., Klasnja, P. *et al*., (2008) Flowers or a robot army? Encouraging awareness and activity with personal, mobile displays, *10th International Conference on Ubiquitous Computing*, Seoul, Korea, 30th May: 54–63.

Department of Health (2002) *Health Survey for England 2000: The General Health of Older People and Their Use of Health Services* [URI http://www.archive2.official-documents.co.uk/document/deps/doh/survey00/ghop/ghop06.htm accessed 16th May 2011.]

Dias, T., Fernando, A., Jaywarna, D. *et al*. (2011) *Case Study: Innovation Scan2Knit Technology*, Advanced Therapeutic materials Ltd. Knowledge for innovation. [URI www.equalworks.co.uk/resources/contentfiles/3759.pdf accessed May 16th 2011.]

Doughty, K. and Dunk, B. (2009) Safe walking technologies for people with mild to moderate cognitive impairments, *Journal of Assistive Technologies*. 3(2):54–59.

Harada, T.E., Akatsu, H. (2003) What is usability – A perspective of universal designing in an ageing society. In: *Cognitive Science of Usability*, Kyoritsu Publisher.

Hultsch, D.F., Hertzog, C., Small, B.J. *et al*. (1999). Use it or lose it: engaged lifestyle as a buffer of cognitive decline in aging? *Psychology and Aging*, 14 (2): 245–263.

Huppert, F. (2003) Designing for older users. Chapter 1. In: *Inclusive Design: Designing for the Whole Population*, Clarkson, P. J., Coleman, R., Keates, S., Lebbon, C. (eds), University of Cambridge.

McCann, J., Morsky, S. and Dong, X. (2009) Garment construction: cutting and placing of materials. In: McCann, J. and Bryson, D.(eds) (2009) *Smart Clothes and Wearable Technology*. Cambridge: Woodhead Publishing Ltd.

Metz, D. and Underwood, M. (2005) *Older, Richer, Fitter: Identifying the Customer Needs of Britain's Ageing Population*. UK, Age Concern Books.

Perman, S. (2004) Banning the rays, *Time*, July 4th [URI http://www.time.com/time/insidebiz/article/0,9171,1101040712-660935,00.html#ixzz19gfvvZnC, accessed 26.02.11.]

Regenold, S. (2011) Touchscreen gloves. *Gear Junkie 2011*: Best in Show, January 31st [URI www.touchtecleather.com/news/gearjunkie-2011-best-in-show, accessed May 16th 2011.]

Rogers, C. (2010) Deflexion protective textile to feature in sailing apparel. *World Textile Information Network*, November. [URI http://ei.wtin.com/article/VDVS5P4CnAs/2010/11/19/deflexion_protective_textile_to_feature_in_sailing_apparel/, accessed May 16th 2011.]

Sheil W.C. (2008) *Hip Fracture Prevention – Hip Protectors*. [URI http://www.medicinenet.com/script/main/art.asp?articlekey=15600 accessed May 16th 2011.]

Sitbon, E. (2010) An open and shut case, WSA: *Performance and Sports Materials*, 16, 2, March/April, 38–39.

Swantko, K. (2002) Adaptive Comfort: Outlast Technologies has found a way to incorporate its patented 'Thermocules' into nylon and polyester fiber to give a broader range of fabrics. *Fabric Development*, Fall: 20–21. [URI www.fabriclink.com/Features/Assets/KA_Outlastfall02.pdf, accessed 25.2.2011.]

Van Langenhove, L. Hertleer, C. and Westbroek, P. (2007). Textile sensors for health care. In Van Langenhove, L. (ed.); *Smart Textiles for Medicine and Healthcare: Materials, Systems and Applications*, Cambridge, Woodhead Publishing Ltd.

Wilson, A. (2010) Energy medicine, Clothtech. In: *Future Materials*, World Textile Publications, October 2010: 14–15.

Wolfe, D.B., and Snyder, R.E. (2003) *Ageless Marketing*. Chicago: Dearborn. ISBN 0-7931-7755-3.

World Health Organisation (2007) *Global Report on Falls Prevention in Older Age* [URI http://www.who.int/ageing/projects/falls_prevention_older_age/en/index.html, accessed 3.1.2011.]

10
Smart high-performance textiles for protection in construction and geotechnical applications

D. ZANGANI, D'Appolonia S.p.A., Italy

Abstract: The use of multifunctional technical textiles represents an opportunity for the construction sector to address some of the limitations of existing structures and to contribute to a radical transformation of the building environment, meeting the expectations of stakeholders and the community, and capable of responding to changing needs. Multifunctional technical textiles are being developed for the reinforcement and structural health monitoring of buildings and geotechnical structures, such as railways and highway embankments and dykes, with the incorporation of sensing elements for localised or distributed measurements.

Key words: structural health monitoring (SHM), multifunctional textiles, fibre optic sensor, fibre reinforced plastic (FRP).

10.1 Introduction

Smart multifunctional materials will be the construction elements of tomorrow. These materials will perform their traditional role (protection, structural reinforcement, filtration, etc.) and at the same time carry data (data porting) or provide information (sensing) for structural health monitoring (SHM). They will also employ sensors, will have communication capabilities, will contain self-healing agents, and have other characteristics to make them multifunctional. As we progress toward this future, there are many challenges to identify and solve. They include the integration of independent technologies into systems, cooperation between multiple disciplines, the formulation of standards and guidelines, and developing the business models that convince both engineers and end users to adopt them.

Textiles provide an excellent candidate for a multifunctional smart material. They are mass produced and inherently low in cost, making them appropriate for wide area civil engineering applications. The industry is extremely competitive, meaning that new innovations are sought after and welcomed because they provide a competitive advantage. The textile manufacturing processes themselves are sensor-integration friendly. Integration techniques include the weaving or warp knitting of sensitive fibres, stitching

based sensors, printable sensors, and coating techniques. Lastly, textiles have broad applications in engineered structures. In geotechnical engineering, they are utilised for soil stability, load distribution, and as filters or membranes. In structural engineering, they are utilised for structural retrofit, seismic upgrade, and blast hardening. Importantly, textiles are often the load-bearing element of composite materials. As such, textile composites can be utilised for the frames and bodies of vessels, aircraft, ships, vehicles, and numerous other applications.

Masonry structures and, in particular, unreinforced masonry structures in areas of seismic hazard, provide the market need for multifunctional reinforcing textiles. Although modern codes, materials, and construction techniques are better adapted for seismic forces, hundreds of millions of existing masonry structures are vulnerable to seismic risk. In many cases, such structures populate urban centres and have cultural heritage value. Retrofit is the only desirable solution.

This chapter will provide information on the latest development of advanced multifunctional textiles for the construction sector. A large part of the work presented comes from the research project 'Polyfunctional Technical Textiles against Natural Hazards' supported by the European Commission under the Framework Programme 7 with grant number NMP2-CT-2006-026789.[1] The contribution of the companies and research institutions performing this work is acknowledged and especially those directly in support of the work mentioned in this chapter, which include Selcom Multiaxial Technology, Alpe Adria Textil and Extreme Materials from Italy, Glötzl, BAM, STFI, the Karlsruhe Institute of Technology and the University of Kassel from Germany, IMMG from Greece, and Smartec from Switzerland.

10.2 Technical textiles for the construction and geotechnical sectors

Textiles suitable for engineering applications can be made of Kevlar, carbon, glass, basalt, and other polymeric fibres. The density, orientation (warp, weft, diagonal), and material composition of the fibres determine the textile's strength and performance characteristics as an integrated system. For geotechnical applications, a wide variety of different products is available. Synthetic raw materials such as polyethylene, polypropylene, polyester, and polyamide are used for geotextiles and geotextile-related products, to comply with stringent cost and durability issues.

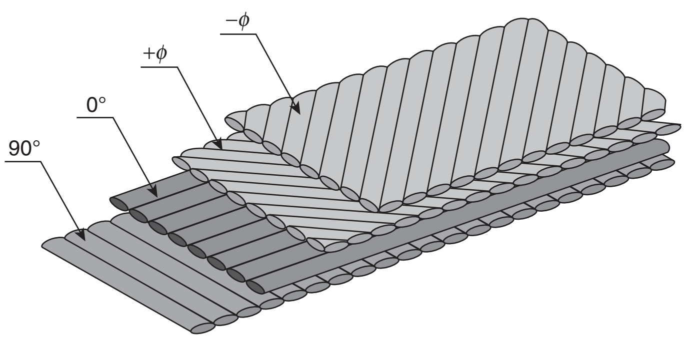
For seismic retrofit using reinforcing textiles, both reinforcing strips and full coverage strategies can be adopted.[2,3] The use of reinforcing strips in grid-like or crossing patterns is more commonplace and building code provisions for their use are available in many countries. Typically, the

reinforcing strips are uniaxial textiles made of a high strength, high stiffness material such as carbon. They are intended to carry loads along their length and are applied with a resin (e.g. epoxy) to create a stiff bond to the underlying structure.[4] The second retrofit strategy is to employ a wide area or full coverage textile using a biaxial or multiaxial structure to carry loads in multiple directions. This strategy is not as commonplace and is maturing in various research programmes. Full coverage solutions aim to employ a low cost fabric of flexible, high strength fibres that dissipate energy through increased structural ductility. For this reason, full or wide area coverage solutions are applied with an epoxy mortar to form a textile composite with the underlying structure.

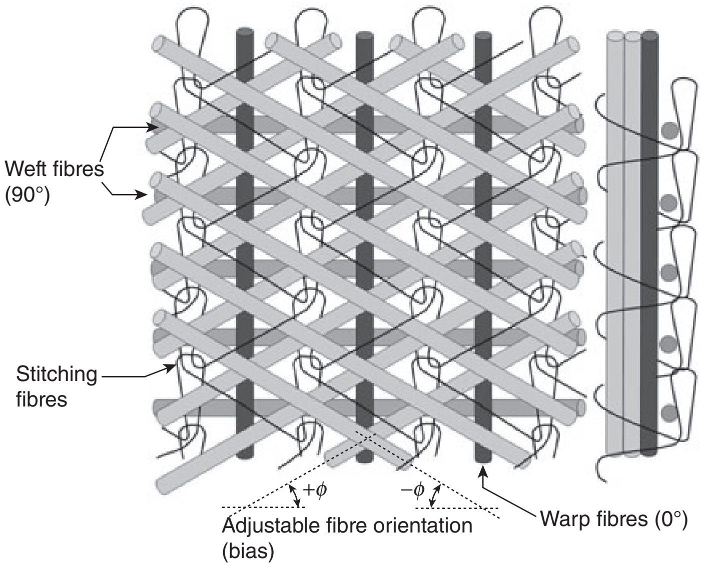
10.2.1 Non-crimp multiaxial fabrics

Non crimp fabrics (NCF) are a particular textile construction, manufactured using warp knitting technology for the production of technical fabrics that are widely used in the composite industry. The particular feature of non crimp fabrics is, as their name suggests, that yarns used in their construction are not crimped, as is case for traditional woven textiles. NCF consist of one or more layers of long fibres oriented along preferred directions, held in place by a secondary non-structural thread. Figure 10.1 shows the structure of a multiaxial fabric produced using the warp knitting system, consisting of four layers of inserted yarns along the warp (=0°), weft (90 °) and bias ($\pm\phi$) directions. In Fig. 10.2, where the same multiaxial structure of Fig. 10.1 is shown, the stitching fibres holding together the various layers are also depicted.

The mechanical properties of NCF composites are controlled by the type, amount, and orientation of the fibre being used. There are today many different types of fibres commercially available to meet the design



10.1 Four-layer multiaxial non-crimped textile.

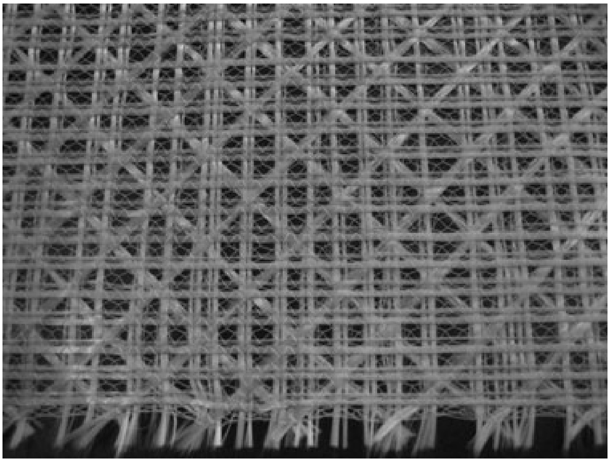


10.2 Schematic of multiaxial warp knit with four layers of inserted yarns and tricot stitch.

requirements of the intended application. The materials more often used for the structural fibres can be glass, carbon, or aramid. The stitching process allows a variety of fibre orientations, beyond the 0/90 woven fabrics. NCFs offer, therefore, the characteristics of oriented strength along the different yarns orientations, something that is preferred in high performance applications. Moreover, multiple orientations can be exploited to obtain a quasi-isotropic reinforcement, which is beneficial for some applications where the main loading directions are unknown. The ability to tailor the fibre architecture allows for more optimised performance, which translates into weight and cost savings.

NCF is the candidate textile architecture for the incorporation of optical sensor fibres because of the absence of crimp in the fibres, which reduces the risk of micro bending of the optical fibre. This would create losses in the fibres and would endanger their function. Another advantage with respect to conventional woven structures is that several layers can be stitched together, including the layer oriented at 0°, where the optical sensor fibres can be placed, and the fabric can be made as thick as desired for the application, so that one single fabric is sufficient. Also, the stitch can be designed to obtain a stable fabric, even with open structures.

Figure 10.3 shows the multiaxial NCF textile Sentex8300 produced by the Polytect partner Selcom Multiaxial Technology, Italy, designed for the seismic reinforcement of masonry walls. Sentex 8300 is made of glass and



10.3 NCF Sentex 8300 produced by Selcom Multiaxial Technology, Italy.

polymer fibres in three directions, has a density of 460 g/m^2 and has nylon 6 tube and polymer optical fibres inserted in the 0° direction during the warp-knitting process. These textiles are the result of a design and optimisation process conducted by the Sächsisches Textilforschungsinstitut (STFI) and evaluated over 120 wall tests conducted at the Karlsruhe Institute of Technology to compare performance under different load scenarios and for different mortar types. As shown in Fig. 10.3 the structure of Sentex8300 is similar to the schematic of Fig. 10.2, having a balanced fibre density along the four main directions (warp, weft and bias), and it is characterised by an open structure for an easy impregnation with the mortar and application to the masonry substrate.

10.2.2 Geotextiles and geogrids

Geotextiles are those fabrics used in geotechnical applications, such as road and railway embankments, earth dykes and coastal protection structures, designed to perform one or more basic functions such as filtration, drainage, separation of soil layers, reinforcement or stabilisation. Almost every geotextile application is multifunctional.

To perform the above functions and in order to satisfy the demanding requirements of cost and resistance required for the intended applications, geotextiles are generically made from polymers: mostly polypropylene and polyester, but also polyethylene, polyamide (nylon), polyvinylidene chloride, and fibreglass (e.g. in roadway substrates). Sewing thread for geotextiles is generally made from any of the above polymers. Using warp knitting

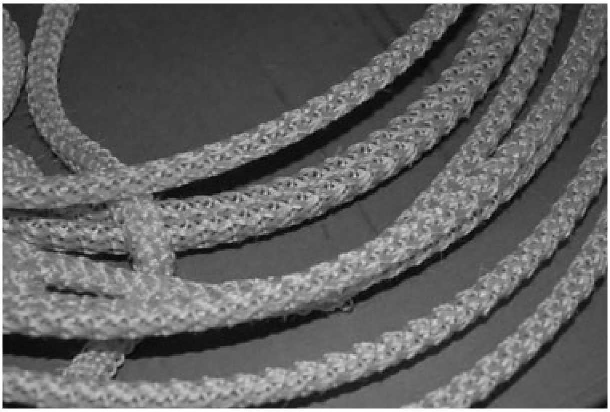
10.4 Multifunctional geotextile produced by Alpe Adria Textil, Italy.

technology to construct geotextiles makes it possible to provide reinforcement with easy sensor incorporation, thus opening up new design opportunities for multifunctional geotextiles (MFGs).[5]

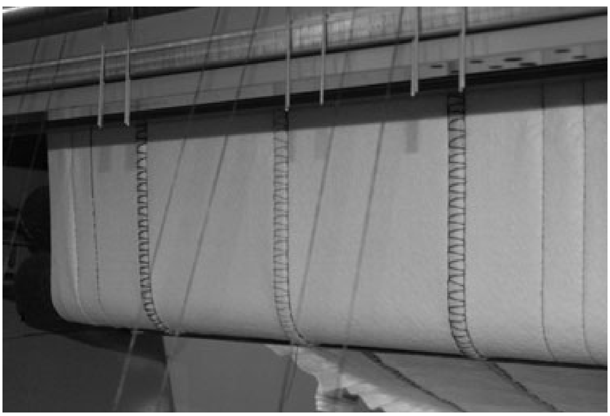
Figure 10.4 shows an example of an MFG produced by Alpe Adria Textil in Italy. In this example the structure is a grid with warp (0°) and weft (90°) fibres, where the warp fibre is characterised by a much higher linear density than the weft yarns, and is, therefore, the major load bearing component of the fabric. The sensors fibres aligned along the warp direction are incorporated into the structure, which is designed to not only carry them but also to protect the sensing fibres from the external environment.

10.2.3 Rope-like structures

Another type of textile structure suitable for the incorporation of sensors is the so-called rope-like structure, shown in Fig. 10.5. In this case, circular warp-knitted technology has been used by the Polytect partner Extreme Materials, in Italy, to produce such ropes. Warp knitting technology was selected to avoid the problem of structural twisting observed when using other knitting technologies. The result is a long textile structure containing a sensor fibre, which is protected from the external environment by the textile threads. Diameters up to about 12 millimetres can be obtained using this technology. Figure 10.6 shows the coupling of the rope-like structure containing embedded optical sensor fibres with nonwoven layers. These textile layers protect the sensor fibres against mechanical impact and increase the contact surface with the surrounding soil.



10.5 Circular knitted multifunctional rope-like structures produced by Extreme Materials, Italy.



10.6 Production of multifunctional geotextile integrating rope structures at Extreme Materials, Italy.

10.3 Incorporating sensors into smart textiles through the use of optical fibres

The smart textile materials described in this chapter are based on the incorporation of sensors into the textile structure, to make the fabric able to be used to interrogate and monitor the status of the structure where it is embedded. Many families of sensors can be used for this purpose. As an example, piezoelectric materials, which produce a voltage when stress is applied, can be incorporated, in the form of fibres, into the fabric, and used as stress and deformation sensors (i.e. when a particular stress is applied to the fabric an electric potential is generated which can be measured and

correlated to the applied stress). Shape Memory Alloys (SMA), in the form of thin wires, have also been investigated as sensing elements embedded in technical textiles used as reinforcement of composites. The Avalon project, for instance, studied the incorporation of SMA fibres in composite structures, mainly to increase their impact resistance, their resistance to damage from repeated impacts. and vibration damping.[6] The use of SMA fibres as sensing elements in the construction was also studied, but the sensitivity of such alloys to temperature variations and the need for temperature compensation solutions required further development.

Fibre optical sensors represent the state-of-the-art sensing technology for structural health monitoring of civil engineering constructions. A large number of applications of fibre optical sensors in such constructions arise because of the established need for structural health assessment (SHA) of highway bridges, but the use of optical sensors for monitoring also extends to offshore structures and pipelines, historical buildings, and geotechnical applications.

10.3.1 Technology and basic concepts

Fibre optic sensors act on the principle of transmitting a light signal through a fibre and measuring the status of the returning or transmitted signal. The change in signal properties is then translated into appropriate quantities that allow the measurement of a wide range of mechanical, physical, and chemical parameters.[7,8] Optical measurement techniques have been studied for more than a century, but they received an impulse in the seventies with the development of low-loss, high-quality, optical-fibre waveguides for the telecommunications industry.

The use of optical fibres as sensing elements for structural health monitoring offers the same advantages as in the field of communication: lower cost, smaller size, more accuracy, greater flexibility, and greater reliability than traditional sensors. As compared with conventional electrical sensors, fibre optic sensors are immune to external electromagnetic interference and can be used in hazardous and harsh environments, as many construction sites are. A very important attribute of fibre optic sensors is the possibility of having distributed or quasi-distributed sensing geometries, which would otherwise be too expensive or complicated using conventional sensors.

The core of the fibre is generally made of silica glass which is surrounded by a cladding (shell) of another glass with a lower refractive index. An external plastic coating is typically added which gives the fibre protection and mechanical strength. Typical core diameters are ~10 microns for single mode fibres (single wavelength light source) and 50, 62.5, and 100 microns for multimode fibres (where a range of wavelengths is used). The larger

core size simplifies connections and also allows the use of lower-cost electronics.

Most common fibre optic sensors used for short and long based temperature and/or strain sensing in civil structures include Fibre Bragg Gratings, Optical Time Domain Reflectometry (OTDR), Fabric Perot, and the SOFO system.[9] In order to provide distributed fibre sensors for mechanical and physical parameters, fibre sensor technologies based on non-linear effects in optical fibres, such as stimulated Brillouin scattering as well as OTDR sensor techniques, are used. Fibre Bragg Grating sensors are suitable for application as point-wise or quasi-distributed sensors. Some of these fibre sensors are based on glass fibres but there are others that are based on polymer optical fibres (POF) – a new and very promising technology – which has a number of advantages, including a higher deformability than glass fibres and therefore a higher suitability to be processed by textile machines.[10]

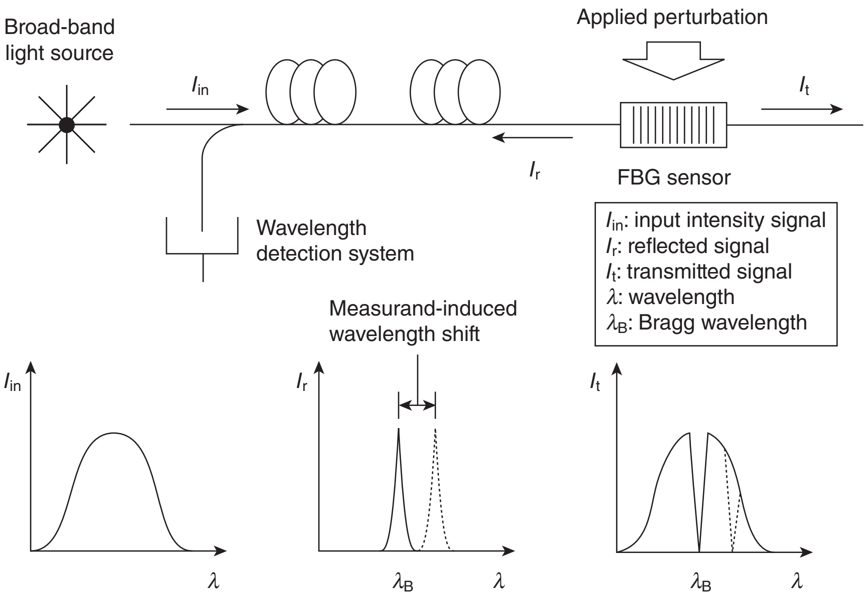
10.3.2 Point and quasi-distributed sensors

A Fibre Bragg Grating (FBG) is a short segment of an optical fibre with a periodically varying refractive index in the core of the fibre. Such segments then act as mirrors, reflecting only a specific wavelength of light propagating through the fibre which is incident on that segment. The rest of the spectrum is transmitted.

The principle of a Bragg grating sensor is shown in Fig. 10.7. It is a local modification to the internal structure of the fibre that causes it to reflect light of essentially one wavelength while allowing all other wavelengths to pass. The perturbation of the grating by the applied stress causes an extension of the fibre and, with that, the increased separation of the grating elements and a change in the characteristic wavelength observed. The wavelength reflected varies, depending on the temperature or strain to which the fibre in the region of the grating is subjected. This wavelength change is detected by means of optical spectroscopy and is interpreted as a change of corresponding physical quantity measured. Bragg gratings are powerful tools for the sensor designer, as they are versatile, and can be multiplexed to create a series of quasi-distributed sensors along a fibre network, as depicted in Fig. 10.8.

10.3.3 Distributed sensors

OTDR uses Rayleigh light scattering in optical fibres to analyse local attenuations along the fibre. For this purpose, a short light pulse is sent into the fibre and the backscattered light is recorded as a function of time or distance, respectively. Any mechanical deformations, such as strain applied to

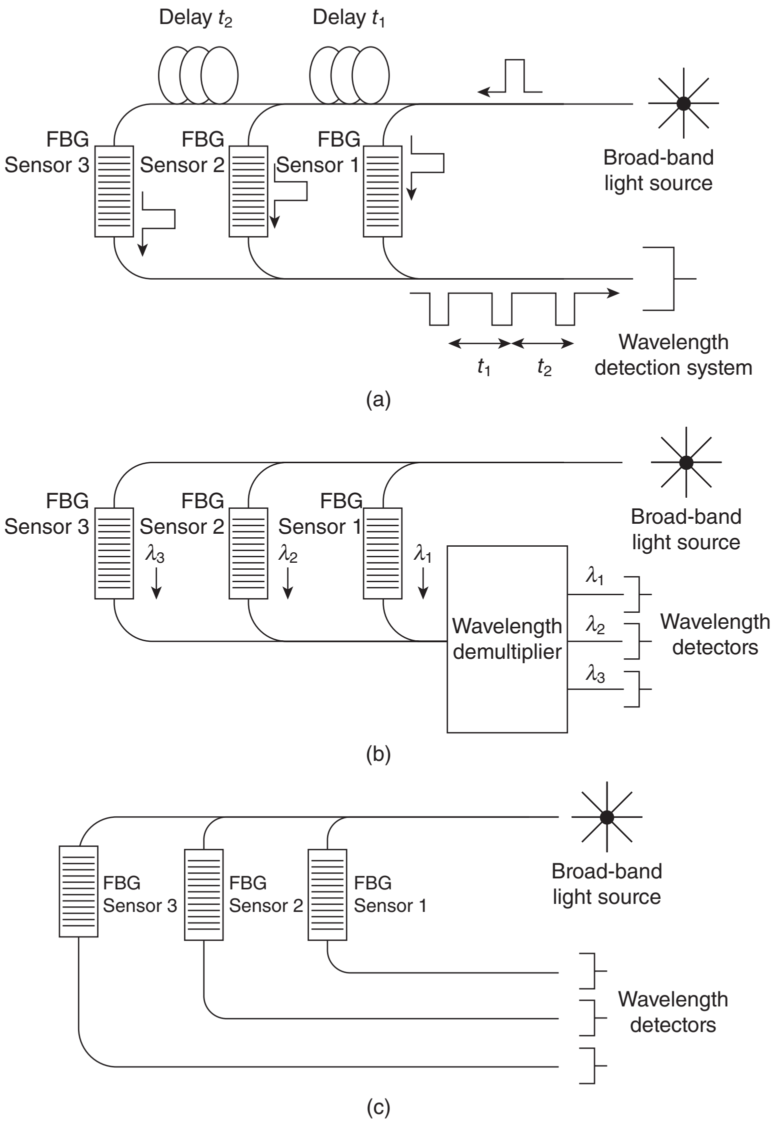


10.7 Principle of operation of a sensor based on a Bragg grating. (Adapted from reference 7, Grattan and Sun, *MRS Bulletin*, 2002.)

any location of the fibre, will change its physical properties (e.g. the refractive index) at this location and will result in a change of the scattered light. Experimental investigations show that strains up to more than 40% can be measured using this sensor technique, with a strain resolution of about 1%.

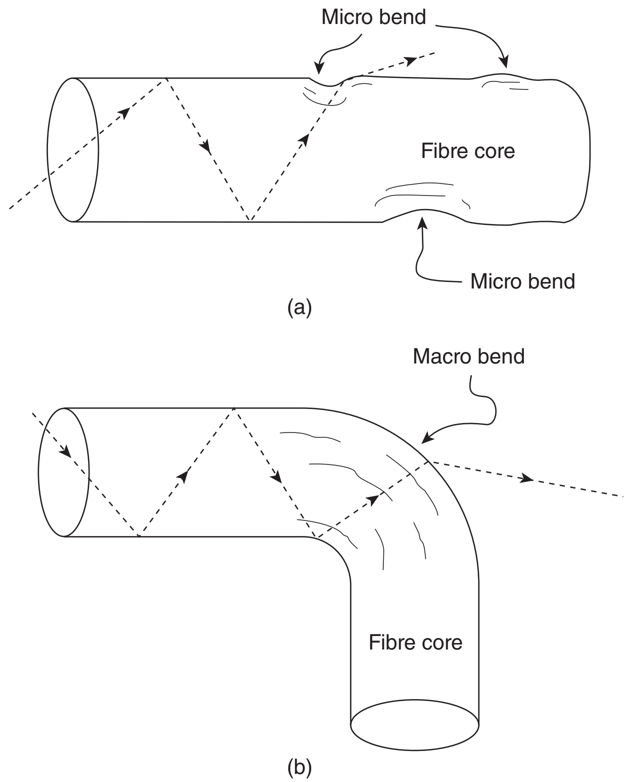
Extrinsic Fabry–Perot Interferometers (EFPIs) comprise a capillary silica tube containing two cleaved optical fibres facing each other, but leaving an air gap of a few microns or tens of microns between them. When light is projected into one of the fibres, a back-reflected interference signal is obtained. This is due to the reflection of the incoming light on the glass-to-air and on the air-to-glass interfaces. This interference can be demodulated using coherent or low-coherence techniques to reconstruct the changes in the fibre spacing. Since the two fibres are attached to the capillary tube near its two extremities (with a typical spacing of 10 mm), the gap change will correspond to the average strain variation between the two attachment points.

Brillouin scattering is an intrinsic property related to the propagation of light in the silica material from which the sensing fibre is made. The Brillouin scattering effect exhibits a well-known and reproducible response to external stimuli, such as temperature and strain, and this method is well suited to distributed measurements. The most disturbing influence on the transmission characteristics of an optical fibre, especially when being



10.8 Multiplexing techniques: (a) time-division multiplexing, (b) wavelength-division multiplexing, and (c) spatial-division multiplexing. (Adapted from reference 8, Webb, *MRS Bulletin*, 2002.)

integrated into technical textiles, is loss due to bends. This is also a problem for the POF OTDR sensor since additional losses limit the effective measurement length and can lead to misinterpretation of the sensor signal. Therefore, bends in the sensor fibre have to be avoided, but also recognised to prevent misinterpretation.[5] Figure 10.9 shows a schematic of the losses



10.9 Schematic of light loss in optical fibres by micro- and macro-bending.

induced by micro- and macro-bending of the optical fibres. It has been observed that bending of the fibres is relatively uncritical for radii greater than about 20 mm. Radii smaller than 20 mm must be avoided during optical fibre sensor integration into textiles and during installation.

10.4 Applications of smart textiles in construction

The benefits of using smart technical textiles in construction are many. They include: the possibility of providing a warning in case of damage in a structure; controlling the construction (for instance, the development of settlement during the construction of a roadway embankment using natural soil); providing data to help select remedial methods to fix problems (for instance by helping identifying the localisation of damage in a structure and its growth, before it could become critical or unstable); advancing the state of knowledge with respect to a new structural design of an unknown structure (for instance in the case of historical buildings where

many uncertainties exist about material status and behaviour); assessing or validating retrofit actions; providing data for structural health monitoring and providing data for life-cycle management of a structure.[11,12] In the following sections, pilot studies on the application of smart materials in the construction sector are reported.

10.4.1 Seismic reinforcement of masonry buildings

The use of advanced materials such as smart textiles for the reinforcement of masonry buildings represents a step forward with respect to the current state of the art and the use of traditional construction materials. Multifunctional textiles offer the opportunity to provide a significant improvement to the structural performance of masonry elements, which are generally characterised by a lack of ductility. The integration of sensing elements makes it possible to conduct the structural health assessment of the structure and be able, after an earthquake, to answer key questions, such as if the structure has been damaged, where the damage is located, how severe is that damage, and to assess the level of structural integrity and safety of the structure.[13]

The state-of-the-art reinforcing technology of seismic retrofitting of masonry structures using composites is based on the bonding of reinforcing fibres, generally unidirectional strips, onto the external surface of the structure to be reinforced, corresponding to the areas where the highest stresses are expected and along the direction of the highest principal stress. A novel approach is based on a full coverage of the surface to be reinforced, using multiaxial reinforcing textiles. Full coverage using multifunctional fibre-reinforced plastics (FRPs) is the approach primarily investigated within Polytect. It is a substantially novel concept, and full coverage with FRP (without monitoring) has already been studied and proved as successful.[14] Both reinforcing strip and wide area coverage textile retrofitting techniques have advantages and disadvantages. Reinforcing strips are fast, lower cost (not the textile itself but its application to an entire structure), and more widely accepted. Disadvantages include concerns over stress concentrations and the potential to increase structural stiffness when this is not desired. Wide area or full coverage solutions offer debris control, help distribute shear forces over larger parts of the structure, and improve structural ductility. However, their application is more time-consuming, labour intensive, and costly. Selection of the appropriate strategy will depend on the particular structure of interest and the goals of the retrofit program. The literature shows clearly and consistently that both strategies dramatically improve structural performance and reduce seismic risk. The use of textiles also prevents additional damage that can result from invasive strategies such as freeze-thaw or drill-induced cracking associated with steel ties.

A uniaxial textile reinforcement was chosen to retrofit a single-story masonry building, specially built in Athens, Greece, at the Institute of Mechanics of Materials and Geostructures (IMMG). After construction, the building's dynamic characteristics were captured using accelerometers and a controllable vibrating mass. The building was then tested unreinforced, as a reference case, up to loading values where significant structural damage was observed . Following this, repair was conducted to fix cracks and to bring the building back to near original condition. As a control measure, the vibrating mass was again utilised to ensure that the retrofitted building had the same fundamental frequencies as it did pre-damage. The building was then retrofitted by applying uniaxial sensor-embedded reinforcing strips with an epoxy resin.

The strengthening of the building by the application of FRP was carried out with the aim of increasing the masonry building strength capacity without increasing the structural displacement at failure, thus increasing the dissipation of energy introduced by the seismic load absorbed and dissipated by the FRP. The aforementioned objectives were realised by adopting a solution able to avoid and/or limit the out-of plane and the in-plane behaviour of the masonry walls, by confining them with FRP strips (vertical, horizontal and diagonal) as depicted in Fig. 10.10. In total, the reinforcement covered around the 20% of the wall's surface. Compared with the unreinforced configuration, the reinforced one provided a much stronger resistance to seismic loads. As a single story structure, the reinforced case essentially became a very stiff box. A peak acceleration of 3.2 g was obtained before damage (significant crack opening), which was an intensity three times greater than that obtained pre-retrofit.

An intelligent composite 'seismic wallpaper' has been developed to be used for the reinforcement, strengthening, monitoring and management of civil infrastructure vulnerable to earthquakes. The textile fibre material type, orientation and density have been optimised for the large forces and complex material behaviour associated with civil infrastructure, masonry, and earthquakes. Multiaxial textile structures are superior in this regard. Moreover, glass and polymeric or hybrid textiles can be used with this concept, rather than carbon fibres, which are characterised by a far higher price and cannot be considered for all applications. The textile is then coated for durability and to enhance the textile–mortar bond interface. It is applied to the structure using a mortar compound.

The composite seismic wallpaper is intended as a full-coverage or wide-area reinforcing solution for unreinforced masonry buildings and structures. The solution is simple, cost effective and easy to apply. When applied as a full-coverage solution and tested in large-scale laboratories, this solution provided over 200% increase in structural strength (max. load) and over 200% increase in structural ductility (max. deformation). Walls vulnerable

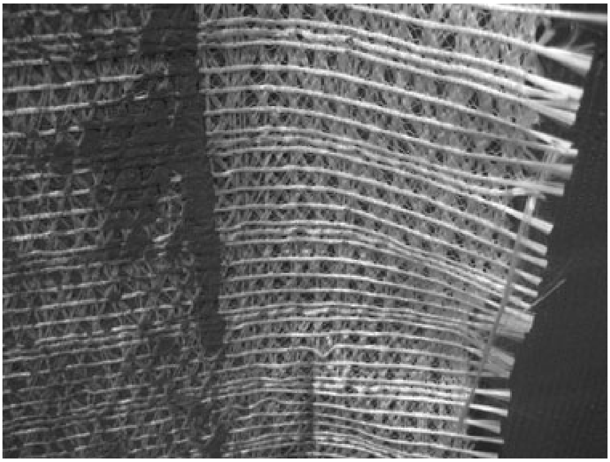
(a)

(b)

10.10 Seismic retrofitting of brick masonry building using uniaxial composite strips and tested at the shaking table of the Institute of Mechanics of Materials and Geostructures (IMMG), Greece.

to brittle behaviour and collapse were being held together even after they cracked.

This composite includes embedded sensors so that measurements can be taken before, during, and after seismic events. These measurements can be static or dynamic (high frequency). Engineers utilise such data to control new construction, to assess and quantify the benefit of retrofit actions, and



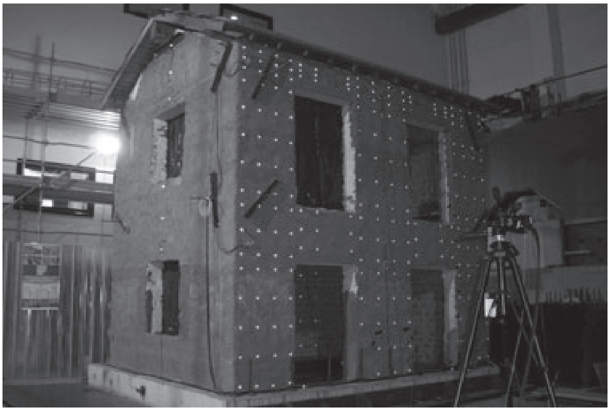
10.11 Example of multifunctional hybrid fabric (Sentex 8300, produced by Selcom Multiaxial Technology, Italy) for the external reinforcement of masonry walls ('seismic wallpaper').

to help manage the structure over time. Figure 10.11 show some examples of multiaxial textiles embedded in the concrete matrix.

The above solution has been validated by conducting a shaking scale test of a masonry building reinforced with the full coverage solution. The test was performed at the European Centre for Training and Research in Earthquake Engineering (Eucentre) in Pavia, Italy, under the 'Seismic Engineering Research Infrastructures for European Synergies' (Series) project and within the Polytect project. The masonry building was manufactured using stones and construction techniques representative of buildings common in the historical centre of central Italy, which was struck by the earthquake of April 2009 when many of such buildings collapsed as a result of the seismic action. The building is a two storey construction, 5.80 m long, 4.40 m width and 5.80 m high. A double-pitched wooden roof covers the building. The roof structure is made by a longitudinal wooden beam and by transversal beams that are simply supported on top of the stone walls. Figure 10.12 shows the phase of application of the multifunctional seismic wallpaper fully covering the external surface of the building, and the building positioned on the shaking table ready for the testing. The reinforcement was applied after two series of shake tests had been performed on the unreinforced structure, leading to extensive damage of the structure, which almost collapsed.

The seismic tests campaign carried out at the Eucentre provided the opportunity to prove the feasibility of the 'seismic wallpaper' solution with distributed and passive reinforcement of masonry structures. It also offered the opportunity to gather localised, as well as distributed, strain

(a)



(b)

10.12 Two-storey stone masonry building: (a) during application of the multifunctional 'seismic wallpaper' and (b) at the shaking table of the European Centre for Training and Research in Earthquake Engineering (Eucentre) in Pavia, Italy.

measurements from the embedded sensors during five seismic tests of increasing base acceleration intensity. Both FBG and distributed fibre optical sensors were tested. In particular, the FBG measurements were processed to analyse the plastic deformations that the building suffered during the tests, and to capture the building dynamics. The latter objective was addressed by processing the FBG data recorded during hammer shock tests, carried out after seismic tests of increasing energy, to identify the relevant building modal parameters (i.e. natural frequencies, mode shapes and damping).

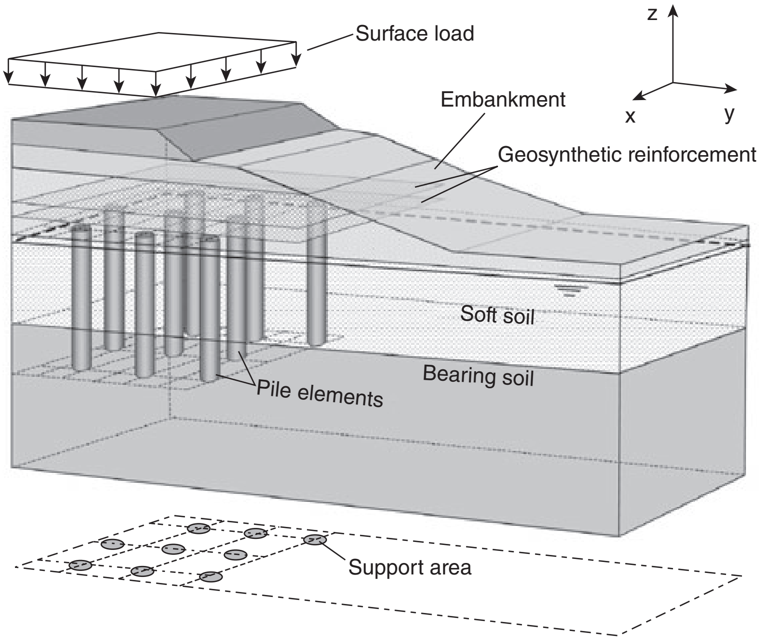
10.4.2 Monitoring of railway embankments

The classical use of geotextiles in embankments on relatively soft soils is to reduce settlement and to increase the bearing capacity and slope stability. Geotextiles are normally placed at the bottom of the embankment, about 50 cm above the original ground surface in one or more layers. In recent years, a new kind of foundation, the so-called 'geosynthetic-reinforced and pile-supported embankment' (GPE) has been developed (Fig. 10.13) and it is now in use in practice. Pile-like elements are placed in a regular pattern through the soft soil down to a load-bearing stratum above which a reinforcement of one or more layers of geosynthetic (mostly geogrids) is placed before the embankment is filled. The stress relief in the soft soil results from an arching effect in the reinforced embankment over the pile heads and a membrane effect of the geosynthetic reinforcement (Fig. 10.13). Figure 10.14 is a schematic representation of the application of multifunctional geotextiles to an embankment for a new roadway placed on a soft soil foundation next to an existing embankment for a railway.

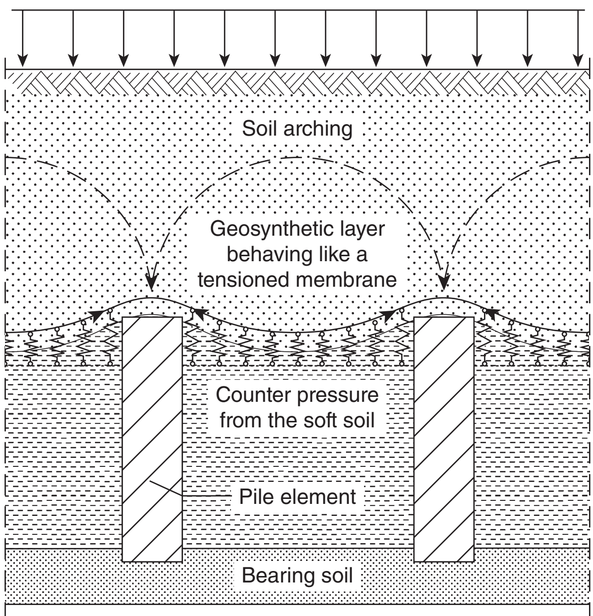
Up-to-date design and construction standards require the installation of systems to monitor the stability and serviceability of geotechnical structures. It is therefore timely to introduce the new robust MFGs in geotechnical engineering practice since they provide, at the same time, both the stability and monitoring functions. In principle MFGs can be applied both to existing and new geotechnical structures. In existing structures, MFGs contribute to the renovation and upgrading of the level of safety to the requirements of today's standards. MFGs can also be used in the extension of existing embankments and dikes, for optimal land utilisation. The monitoring system associated with MFGs will contribute to the mitigation of natural hazards. Mitigation of geological natural hazards includes protection by strengthening and stabilisation of the existing structures and monitoring their performance, with the possibility of the infrastructure owner being alerted by an alarm before structural failure occurs. This is achieved by setting predetermined values for selected critical parameters.

MFGs are equally important in newly constructed geotechnical structures, where they are not intended to replace the standard geotextile, but rather to be used as an additional element that provides added strength and structural health monitoring. Since the application of geosynthetics is relatively new in geotechnical engineering, the monitoring and inspection of such construction is another challenge. In particular, the performance of geosynthetics under dynamic loads and their long-term behaviour has not been fully assessed at present.

A demonstration of the application of MFGs was performed within the Polytect project on a curve of a railroad near Chemnitz in Germany, characterised by a high volume of rail traffic. The portion of the

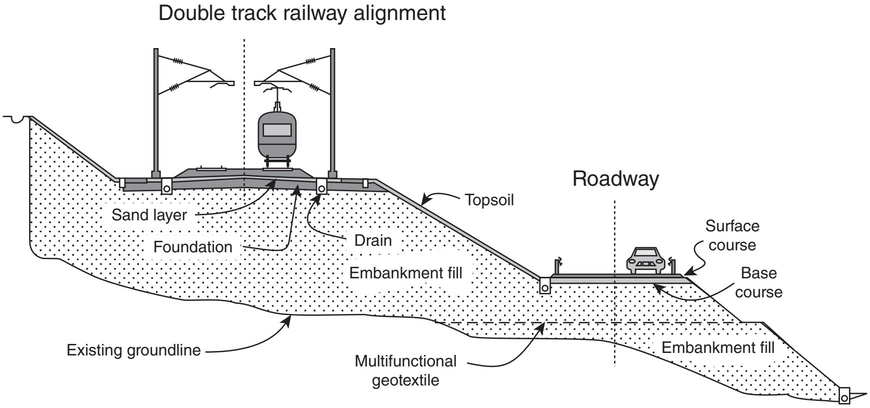


(a)



(b)

10.13 (a) Geosynthetic-reinforced, pile-supported embankment and (b) mechanisms of load transfer.



10.14 Typical combined embankment section with multifunctional geotextiles for stabilisation and monitoring of foundation deformation.

10.15 Multifunctional geotextiles.

embankment of interest for the test was more than 100 years old and was selected as it was to be reconstructed. Figure 10.15 shows the multifunctional geotextiles that were produced for the test. This was carried out under the supervision of the Sächsisches Textilforschungsinstitut e.V. (STFI) in Germany, in cooperation with Extreme Materials in Italy (producer of the textiles), SL-Spezialnähmaschinenbau Limbach in Germany, the University of Kassel, and the Federal Institute for Materials Research and Testing (BAM) in Germany. The sensor-embedded textiles survived perfectly the harsh installation steps (Fig. 10.16) and were periodically interrogated at the end of the embankment reconstruction work to check for the occurrence of any deformation or settlement in the embankment that might have been induced by the railway traffic. This test proved the feasibility of using optical fibre sensors for monitoring railway embankments.

(a)

(b)

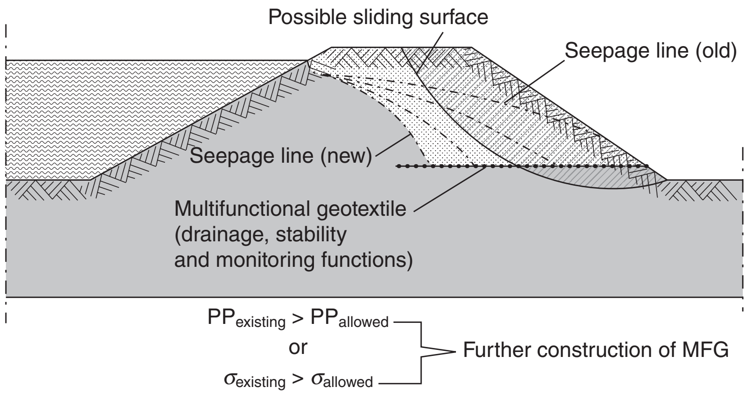
(c)

10.16 Installation steps of multifunctional geotextile for monitoring deformations of a railway embankment near Chemnitz, Germany. (a) Positioning of the sensor-integrated geotextiles over the foundation soil; (b) soil compacting; (c) completing the embankment with the upper layer of soil over geogrids.

Distributed fibre sensors having a length of many kilometres, and, embedded in geotextiles, have the potential of monitoring extremely long railway corridors with the possibility of being able to alert the railway infrastructure manager about anomalies along the line.

10.4.3 Applications in dykes and for coastal protection structures

Dykes are prone to stability problems from increasing flood levels during rainy seasons. Climate change has threatened many areas around rivers and coastal areas, leading to an increased risk of flooding. The floods in Romania, India, China and in some Asiatic countries in recent years, and the flood catastrophe in Germany and the Czech Republic in 2002 along the river Elbe, are examples of this problem. Flooding may occur either by



10.17 Possible arrangement of multifunctional geotextiles to avoid dyke failure during high water level. PP, pore pressure; σ, soil strength.

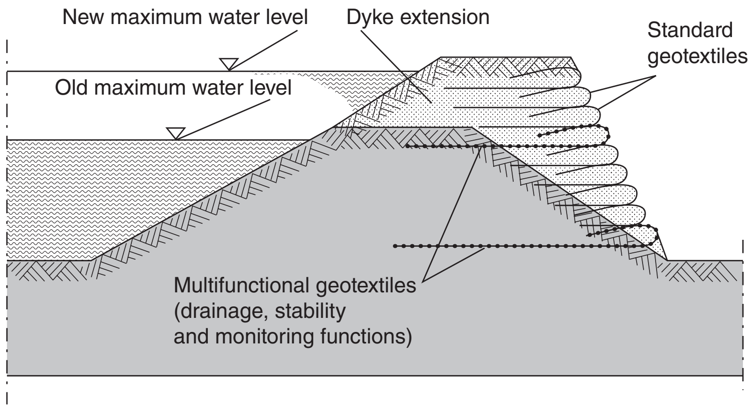
overflowing of the existing dykes or due to dyke failure. Most of the existing dykes are more than 50 years old and were constructed using locally available materials; the technologies that were available at the time of their construction might not necessarily satisfy today's safety requirements. Therefore, a cost effective retrofitting technique for increasing the stability of the structure and the introduction of an integrated monitoring system for the control of the stability conditions, would be an important step towards the mitigation of flood damage and its consequences.

The introduction of MFGs within the structure of the dyke will lower the seepage line and hence increase the stability of the dyke slope, will serve as a reinforcement, and will provide information on the strain distribution in the dyke body. Figure 10.17 illustrates the function of MFGs in river and coastal dykes. The monitoring system serves to supervise the safety of the dyke so as to inform the infrastructure owner of abnormal behaviours. Depending on the monitoring results, the stability of the dyke can be estimated at any time, and additional structural elements can be installed if necessary.

Global climate change tends to increase the water level in rivers and basins. Therefore, the height of existing dykes should be increased accordingly. The use of a reinforced slope can be the fastest and most cost effective method of increasing the height of an existing dyke (Fig. 10.18). A slope of up to 80° is possible with this type of construction. The other advantage is that no extra land area is required for the dyke extension.

10.4.4 Soil stabilisation and subsidence protection

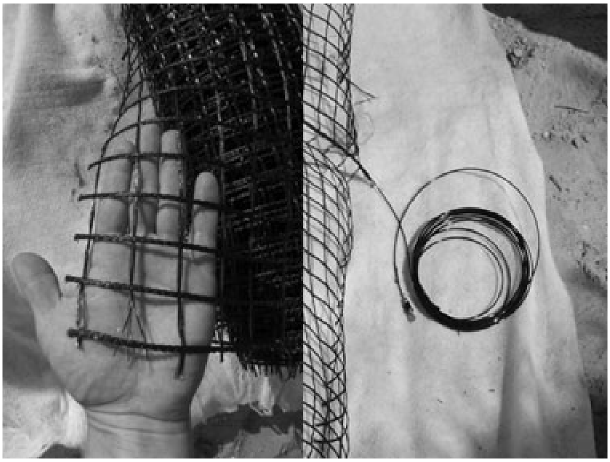
Another application of MFGs is for soil stabilisation and for the monitoring of creeping and landslide slopes. The sensors incorporated within the MFG



10.18 Extension of existing dyke with multifunctional geotextiles.

allow the monitoring of strain and soil settlements. In addition, the geotextile structure can be designed to provide a contribution to the stability of the slope or to counteract erosion of denuded slopes. In slopes with a safety factor close to 1.0, the application of surface MFG would allow the recording of early warning signs, such as tension cracks, before slip failures would occur. In such cases, the cost of large-scale removal of the unstable soil and replacement with more stable granular material can be prohibitively high and the use of surface MFG, properly anchored to the stable soil, could be a cost-effective solution.

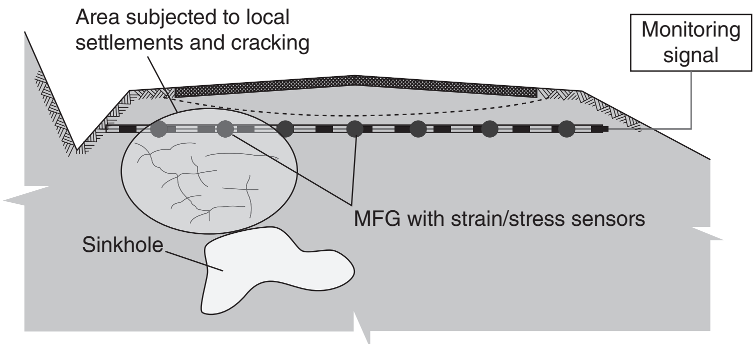
The suitability of surface MFG for monitoring of slopes was demonstrated by Glötzl GmbH, Germany, at the Belchatow brown coal mine near Lodtz in Poland.[15] For this field test an MFG produced by Alpe Adria Textil, Italy, having a length of about 10 metres and a width of 4 metres was used. This was equipped with a plastic optical fibre sensor (POF) (Fig. 10.19). The installation steps were as follows (Fig. 10.20): subgrade preparation by green removal and levelling, product unrolling and placement over the prepared substrate, tensioning and fixing the geotextile to stable soil, placement of cover fill, sensor interrogation to establish the reference zero-measurements, and protection of the sensor ends using protection boxes for future measurements. The sensor interrogation principle was based on the use of the Optical Time-Domain Reflectometer (OTDR) technique and was carried out in cooperation with the Federal Institute for Materials Research and Testing (BAM), Germany. One of advantages of POF fibres over glass fibres for this application is the higher strain they can tolerate, which could be up to 40%: this is highly desirable in geotechnical applications. One of the drawbacks of POF fibres is that soil creep and POF relaxation influence the sensor readings, and further research is needed to separate such effects from the actual settlement values.



10.19 Multifunctional geogrid produced by Alpe Adria Textil, Italy.

10.20 Testing of multifunctional geotextiles for monitoring of sliding slope at Belchatov coal mine, Poland, by Glötzl GmbH, Germany.

There are many inhabited areas over or near coalfields or disused mining areas. The subsoil of these areas is characterised by voids, which can remain stable or can deteriorate and lead to surface subsidence. Changes in the vertical stress or depth of cover as the result, for instance, of the construction of highway embankments over the area, can accelerate this process. As subsidence can occur without warning, it can pose a risk to life. Similar problems may occur with natural cavities formed by differential solution of rock by underground waters: these cavities are known as sinkholes. Such effects create an indentation in the Earth's surface which can span a small



10.21 Application of multifunctional geotextile for monitoring settlement in embankment due to the formation of sinkholes.

area, as in a sink hole or a large area: in the latter case, collapse may be hardly noticed. MFG can prove to be a cost-effective safety measure, as depicted in Fig. 10.21. As illustrated in this figure, MFG can mitigate the surface subsidence, identify the area where the subsidence is localised and control the rate at which subsidence is propagated, thereby preventing a sudden and potentially very dangerous collapse.

Smartec SA, Switzerland, producer of monitoring systems based on fibre optical sensors, in cooperation with the textile company Extreme Materials in Italy, have conceived a new product, called SMARTgeotex. It comprises an optical fibre that is protected from the surroundings by being incorporated inside a rope-like structure. This product protects the optical fibre, increases the sensitive detection area and averages the loadings that are transmitted to the optical fibre. In this way, local settlement can be detected and, at the same time, small effects due to non homogeneous conditions of the soil (e.g. small stones pressing the cable) can be averaged.

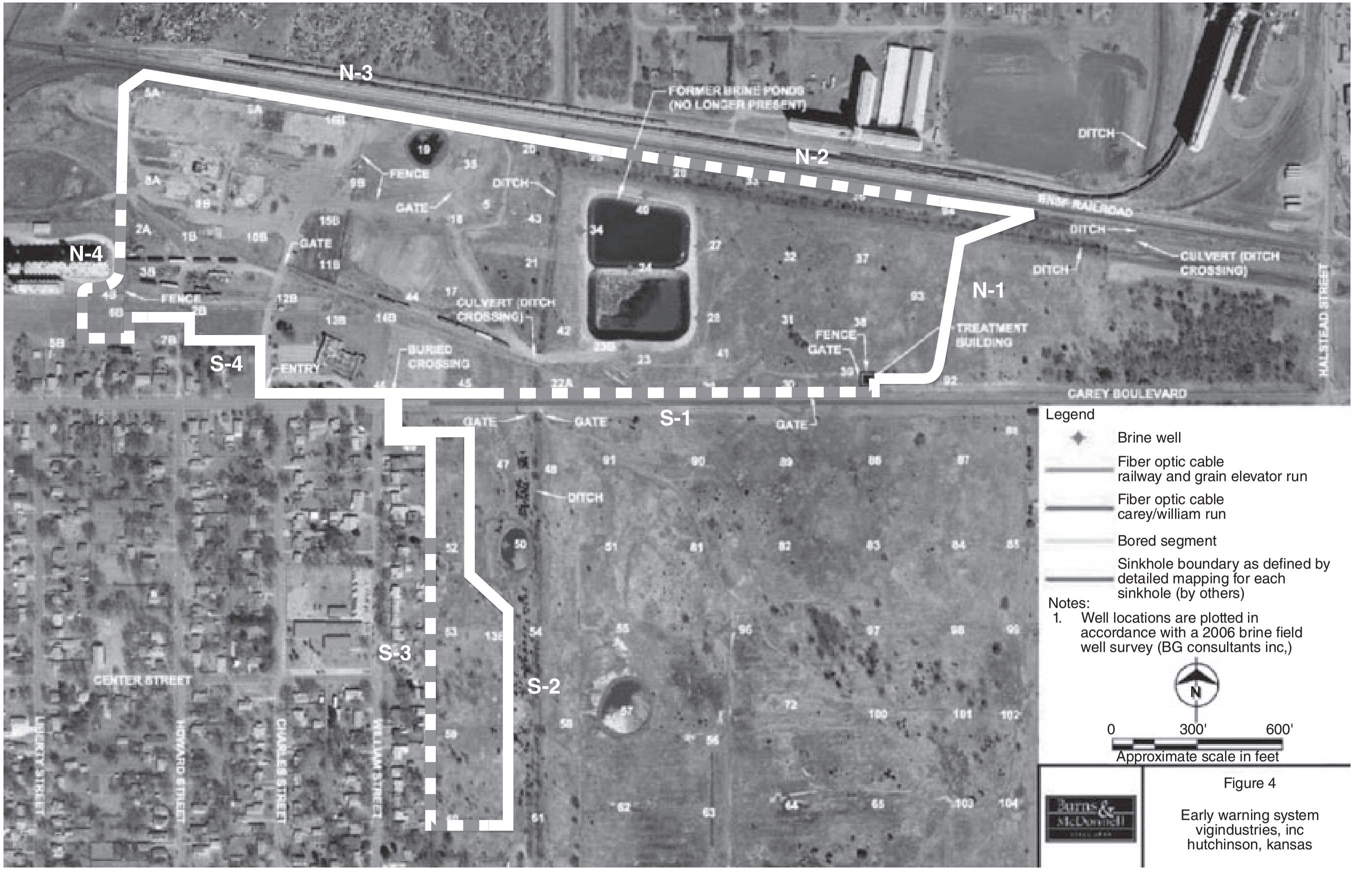
Tests on SMARTgeotex rope have been carried out in cooperation with Kassel University, Germany, where the sensor was calibrated. An opportunity for the application of the SMARTgeotex rope sensor was provided in response to a request for monitoring solutions for subsidence problems in Hutchinson, Kansas. In 1914, subsidence within the salt works of the Joy Morton Salt Company southwest of Hutchinson affected an area 150 feet in diameter, with a vertical depression of 15 feet, demolishing part of the plant. In 1974, a sinkhole 300 feet in diameter formed, in three days, south of the same plant, leaving railroad tracks suspended in the air (see http://www.kgs.ku.edu/Publications/Bulletins/214/). The surface subsidence areas in Kansas are related to salt removal and have a common history of slow development over a period of months and years. However, where near-surface materials consist of water saturated unconsolidated sands and gravels, and the underlying bedrock layers are breached, a surface sinkhole

can form in a few hours or days. There have been four cavern collapses in this area over a 77-year span: two occurred in 1978, one in 1990 and one in 2005. A study conducted by VigIndustries, the owner of one property to the north east of the Careyville residential area in Hutchinson, observed that the collapse of any given cavern could not be predicted accurately and collapses did not occur at regular intervals. It was also observed that early warning signals, such as creep, road sag and subsidence, could occur over hours, days or weeks. VigIndustries decided therefore to proceed with additional investigations and evaluate possible remedies. The SMARTgeotex technology offered a chance for an effective distributed monitoring system for early warning sign detection. The plan of the monitoring system is depicted in Fig. 10.22 while Fig. 10.23 shows the excavation of the trench and the positioning of the sensor rope. The installation required the use of additional measures for the protection of the sensing cable from animals (desert dogs).

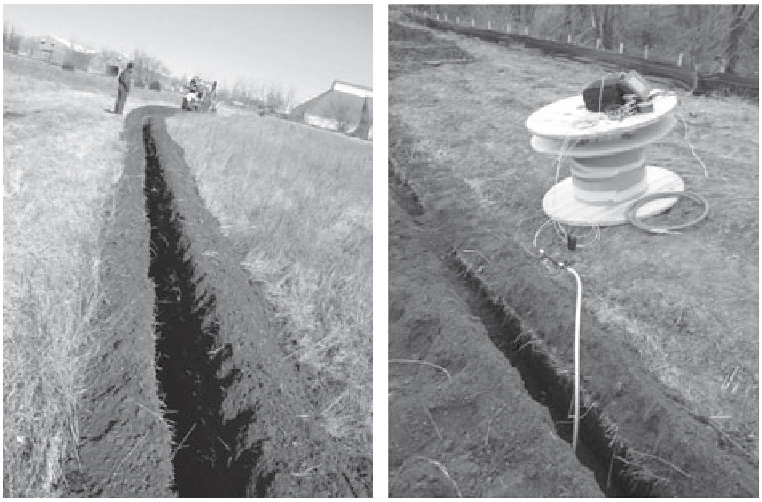
10.5 Future trends: the Industrial Smart Materials Applications (ISMA) initiative

Ensuring the safe operation of existing ageing infrastructure and designing new civil infrastructure that incorporates SHM to increase safety and to lower life-cycle costs are both challenges that are faced worldwide. For this reason, collaborative international partnerships that exchange information, reduce redundancy, and share best practices are highly desirable. The Intelligent Manufacturing Systems (IMS) Program is one such platform that encourages industry-led international research and development to create the next generation of manufacturing and processing technologies. Within the IMS Program, Manufacturing Technology Platforms (MTP) are 'focused knowledge-sharing platforms for researcher groups that are already engaged in a specific R&D domain'. To reduce overlap and duplication in research that is conducted, an MTP Initiative seeks cooperation to conduct joint research in projects that are already running. This ultimately saves resources for the 'golden nuggets' of their research, and finds common solutions to manufacturing challenges in the process. Thus, the main deliverable of an MTP is research conducted through the 'joining together of on-going projects, thus eliminating work duplication, or stimulating new collaborative research.'.[16]

Using Polytect, which focuses on sensor-embedded textiles for geotechnical and masonry applications as one underlying project, the company D'Appolonia in Italy has formed an MTP key technology initiative entitled 'Industrial Smart Material Applications (ISMA): Manufacture, Build, Monitor, Assess, Predict, and Manage'. The aim of this initiative is to form an international collaborative platform focused on sharing knowledge and



10.22 Plan of the installation of the SMARTgeotex rope sensors in Hutchinson, Kansas.



(a) (b)

10.23 Excavation of the trench for the installation of the smartgeotex rope in Hutchinson Kansas. (Courtesy of Smartec, Switzerland.)

expertise related to successful case-studies and test-beds for all types of smart materials across all types of applications. The intention is to leverage best practices between different sectors and different regions to reduce redundancy, create new research opportunities, and open new markets.

The growing ISMA consortium consists of more than 30 members, including industrial partners, universities, and research centres. The industrial companies bring special value into the consortium and it is their presence and manufacturing activity that sets ISMA apart from other working groups. These for-profit organisations must focus on products compliant with norms and standards that lead to customer sales. They must also solve the manufacturing challenges associated with creating new materials, which often require modification to existing equipment, production trials, testing, and validation. Industries represented within ISMA include general engineering consulting, structural inspection, and instrumentation companies, geotechnical instrumentation and consulting companies, SHM hardware providers, SHM consultants, textile manufacturers, and composite producers. In total, these companies have experience monitoring over 3000 projects, with exposure to civil infrastructure, mechanical equipment, and naval vessels.

10.6 Sources of further information and advice

- Polytect: Polyfunctional Technical Textiles against Natural Hazards, www.polytect.net

- Intelligent Manufacturing System (IMS) Initiative and Manufacturing Technology Platform (MTP) Program, http://www.ims.org

10.7 References

1. D. Zangani, 2008, ‘Multifunctional textiles for protection against natural hazards’, in *Advances in Science and Technology*, 56, 601–608.
2. D. Zangani, M. Scotto, P. Corvaglia, J.C. Münich, 2007, ‘Rehabilitation and seismic reinforcement of masonry structures with multifunctional composites’, *Compositi Magazine*, 5, 52–56.
3. T.B. Messervey, D. Zangani, C. Fuggini, 2010, ‘Sensor-embedded textiles for the reinforcement, dynamic characterisation, and structural health monitoring of masonry structures’, *Structural Health Monitoring 2010*, Sorrento, Naples, June 28–July 4.
4. L.C.Hollaway, P.R. Head, 2000, ‘Composite materials and structures in civil engineering’, Volume 6 of *Comprehensive Composite Materials*, Elservier.
5. S. Liehr, P. Lenke, K. Krebber, M. Seeger, E. Thiele, H. Metschies, B. Gebreselassie, J.C. Münich, L. Stempniewski, 2008, ‘Distributed strain measurement with polymer optical fibers integrated into multifunctional geotextiles’, in *Optical Sensors 2008*, Vol. 7003 of *Proceedings of SPIE*, April 2008, Article No. 700302.
6. Pappadà S., P. Gren, K. Tatar, T. Gustafson, R. Rametta, E. Rossini and A. Maffezzoli, 2008, ‘Mechanical and vibration characteristics of laminated composite plates embedding shape memory alloy superelastic wires’, *Journal of Materials Engineering and Performance*, 18, 5–6, 531–537.
7. K.T.V. Grattan and T. Sun, 2002, ‘Optical-fiber sensors: temperature and pressure sensors’, *MRS Bulletin*, May, 27, 5.
8. D.J. Webb, 2002, ‘Optical-fiber sensors: an overview’, *Materials Research Society Bulletin*, May, 27, 5.
9. A. Del Grosso, D. Zangani, T. Messervey, 2008, ‘Smart Structures with fibre-optic technologies’, *Seismic Engineering Conference Commemorating the 1908 Messina and Reggio Calabria Earthquake. AIP Conference Proceedings*, 1020, 162–169.
10. S. Liehr, P. Lenke, M. Wendt, K. Krebber, M. Seeger, E. Thiele, B. Gebreselassie, C. Munich, 2009, ‘Polymer optical fiber sensors for distributed strain measurement and application in structural health monitoring’, *IEEE Sensors Journal* 9, 11, 1330–1338.
11. T.B. Messervey, D. Zangani, S. Casciati, 2009, ‘Monitoring technologies: progressing from theory to application’, *Proceedings of 4th International Conference on Smart Structures and Materials*, 1699–1706.
12. A. Marr, 2007, ‘Why monitor geotechnical performance?’, *Proceedings of the 7th International Symposium on Field Measurements*, 24–27.
13. T.B. Messervey, D. Zangani, D.M. Frangopol, 2009 ‘Multifunctional materials: from manufacturing to application, planning for the integration of reliability and risk concepts’, *Proceedings of the 10th International Conference on Structural Safety and Reliability, ICOSSAR*, 13–17 September 2009, Osaka, Japan.
14. J. Jai, G.S. Springer, L.P. Kollar, H. Krawinkler, 2000, ‘Reinforcing masonry walls with composite materials-model’, *Journal of Composite Materials*, 24, 18, 1548–1581.

15. Presentation of Glötzl GmbH during *VI. International Brown Coal Mining Congress* in Belchatow, Sportshotel, 18–20. May 2009.
16. T. Messervey, D. Zangani, 2009, 'The ISMA initiative: collaborative international research for the advancement of structural health monitoring', *Proceedings of the 7th International Workshop on Structural Health Monitoring*, Stanford University, Stanford, CA. September 9–11.

11
Smart textiles for the protection of armoured vehicles

S. NAUMAN, Institute of Space Technology, Pakistan,
I. CRISTIAN, Technical University Gheorghe Asachi of Iaşi,
Romania and F. BOUSSU and V. KONCAR,
University of Lille, France

Abstract: The requirement for weight reduction encourages the use of composite materials which are lighter than steel for similar mechanical performance. In the field of vehicle armour, existing solutions can be improved by the introduction of new composite materials in combination with steel or ceramics. One of these solutions may lie in the use of three-dimensional (3D) textile structures, in particular a multi-layer fabric called 3D warp interlock, using different types of high performance fibres. A new textile composite solution is presented in this chapter. To enhance on-line measurement of mechanical stresses during impact, a fibrous sensor has been developed to better understand the *in-situ* behaviour of the target.

Key words: textile composite, yarn sensor, vehicle armouring, composite material.

11.1 Introduction

In all areas of transportation, strengthening of vehicles is required in order to protect some parts or the entire surface of the structure against impact. In the field of civil aerospace, satellites need to resist very high speed, small size meteorites. Commercial and other civilian aircraft need to be protected against bird strike and other atmospheric threats. Civilian vehicles such as car structures are designed to resist front and side crashes on static walls under certain speed limits, while high speed trains are subjected to animal and stone impacts to test their impact performance prior to commissioning. Finally, marine transport, such as high speed boats, have to cope with the impact of floating hazards such as wood or icebergs. For military applications, vehicles are designed to resist conventional ammunition with a range of mass and velocity, and also non-conventional projectiles contained in Improvised Explosive Devices (IEDs) (Wilson, 2005).

Two different approaches exist for vehicle armour. The most developed approach, which is called the 'up-armouring' of vehicles, consists of the application of existing solutions to provide impact protection to the structure surface. The less developed approach tends to integrate the protection

material solutions inside the structure during the design phase. Traditional materials used for vehicle armour include steel, aluminium, titanium, depleted uranium (DU), and bullet-proof glass, ceramic and composite materials.

The Kyoto Protocol led the European platform ACARE (Advisory Council for Aeronautical Research in Europe), for example, to define ambitious strategic objectives (with respect to the effects on the environment) for air transport systems (ACARE, 2008). These goals include reduction by half of current average noise and CO_2 emission per passenger per kilometre. These goals, in turn, require weight reduction in aircraft. Similar targets for weight reduction are required in all areas of transportation whenever possible, keeping in view performance and economic constraints in order to optimise the consumption of energy. Energy consumption can be optimised by the replacement of steel parts by high performance composites. Moreover, the higher the speed of vehicles, the greater is the requirement for lighter material solutions.

Composite materials developed for aerospace, aeronautic, automotive, railway and marine applications are designed to be the best as regards technical performance and weight reduction, coupled with an appropriate price for the target market. Composite materials provide an attractive solution for up-armouring, as well as for the integrated armour of vehicles; in addition to mass reduction. Textile composites reinforced with aramid and polyethylene fibres are already used for up-armouring of vehicles. However, one of the weak points of these materials is their damage tolerance (shocks and delamination), which is associated with the difficulty of detecting damage, since impact damage is harder to see, unlike with steel. This lack of knowledge is compensated for by designing thicker, oversized parts, which contributes to undue weight gain. This design issue can be addressed by designing fibrous architectures having 3D reinforcement, which confer satisfactory mechanical properties in all directions.

Research is being carried out in order to better understand the failure mechanisms of armoured solution during ballistic impact. Improved understanding of different failure modes will lead to the development of better and more efficient armour. One of the possibilities in this regard is the integration of an intelligent sensor network in such a composite. This sensor network should be able to give real time, on-line information about deformation, and extent of damage and energy dissipation in the case of ballistic impact.

Some studies demonstrate that composites reinforced with 3D textile structures have high ballistic impact damage resistance and low velocity impact protection (Chou *et al*., 1992a; Miravete, 1999; Bahei-El-Din and Zikry, 2003). It has also been shown that 3D structural composites have better performance compared to two-dimensional (2D) laminates

(Baozhong *et al*., 2005). According to impact studies carried out on 3D-woven composites (Chou *et al.*, 1992b; Baucom and Zikry, 2005; Khalid, 2006; Naik and Sekher, 2000), their high performance is mainly due to their greater resistance to delamination (Chou and Ko, 1989; Mouritz *et al*., 1999). 3D angle warp interlock fabric offers higher strength and damage resistance as a consequence of their interlaced structure of warp and weft threads between the adjacent layers (Ko, 1989).

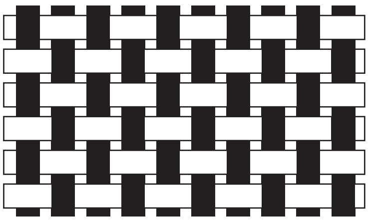
Low velocity impact properties of 3D woven composites are important for their various applications. This type of loading can occur when tools are dropped on the surface of a composite, or when the material is impacted by debris, fragments, or projectiles. In a recent study, two types of 3D woven basalt/aramid hybrid composites with similar fibre volume fractions and dimensions were tested. These were an inter-ply hybrid and an intra-ply composite. Post-mortem photographic analysis indicated that the inter-ply hybrid failed in layer-by-layer mode, leading to much larger energy absorption, while the intra-ply composite showed a brittle mode, resulting in significantly lower energy absorption (Wang *et al*., 2008). It should also be mentioned here that 3D textile structural composites are much tougher between layers because many reinforcing yarns exist in the through-thickness direction. All of these research studies show the particular relevance of 3D composites for ballistic impact protection.

In order to show the efficacy of a 3D textile composite material, a special target has been designed using 3D woven composite material made with high performance fibres. The proposed solution is detailed in the sections giving the ballistic performance for given ammunition under testing conditions specified in the appropriate standard. At this stage of the authors' research, the *in-situ* performance of the protection during impact has not yet been evaluated. This will be possible only after the final development of adapted sensor yarns, whose technical characteristics are described later in this chapter.

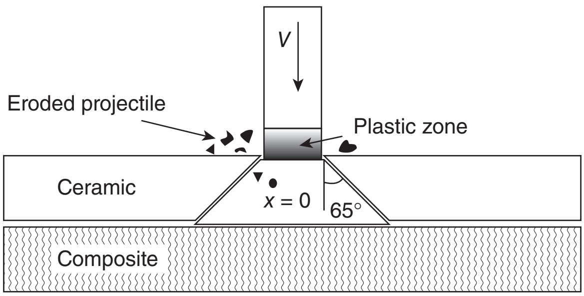
11.2 Understanding impact behaviour

The most used textile structures in technical applications are laminated, nonwoven, woven and knitted fabrics. Laminated or woven structures are mostly found in ballistic soft protection. In hard protection, a combination of textile composite materials and steel or ceramic plates is usually preferred. Such kinds of materials have to be efficient and resistant not only against impact but also against blast effects. Currently, 2D plain weave structures represent effective ballistic protection. They offer a low-cost method of producing large volumes of material, with similar mechanical resistance to that obtained with laminates of unidirectional tapes (Fig. 11.1).

Ceramics are used in ballistics to protect against the hardest of projectiles. The goal of ceramics is to deform the projectile in order to increase the



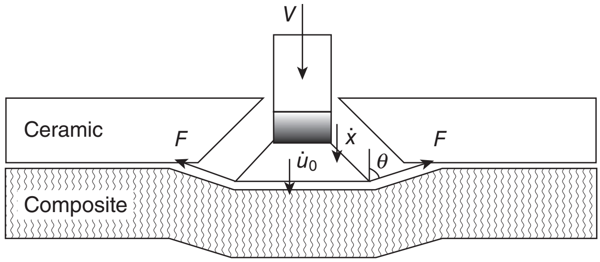
11.1 Plain weave fabric.



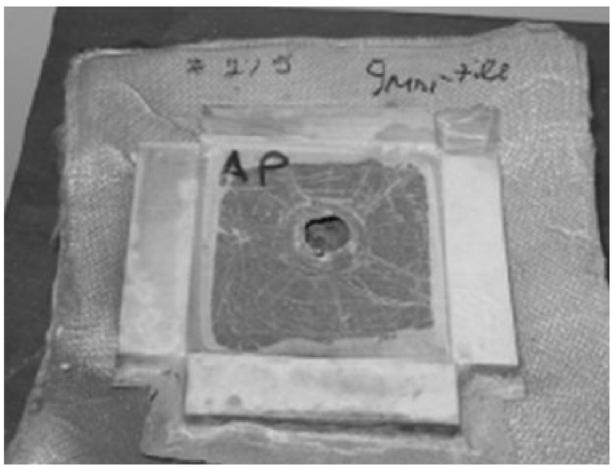
11.2 Configuration at the end of the first phase. *V*, impact velocity of the projectile; *x*, velocity of the plastic zone of the projectile equal to zero at the initial impact time, $t = 0$.

surface of the threat that is in contact with the material (Feli and Asgari, 2011). The optimum combination of ceramic/composite cannot be established: it depends on which kind of threat has to be stopped. Different ceramic composite constructions are recommended depending on the type of threat (Medvedovski, 2010).

When a projectile hits the target, the first phase is the destruction of the jacket surface: the ceramic is not penetrated. During this mechanism, a cone is formed through the ceramic (Fig. 11.2) due to the compressive wave formed, which is reflected as a tension wave. This tension wave induces cracking of the brittle ceramic. Then, during the second phase, the projectile penetrates (Fig. 11.3) and the whole structure becomes involved in slowing down the projectile. The fracture spreads all around the cone and the projectile is rubbed away. This erosion is induced by the difference between the velocity at the rear of the projectile and the head, which is the interface of the projectile with the ceramic. This difference causes a pressure on the projectile. During these two phases, the projectile loses some kinetic energy. The cone of deformation allows the spreading of the remaining energy over a larger area (Fig. 11.4). By doing so, the backing face of the composite may absorb the residual energy (Gonçalves *et al.*, 2004; Shokrieh and Javadpour, 2008).



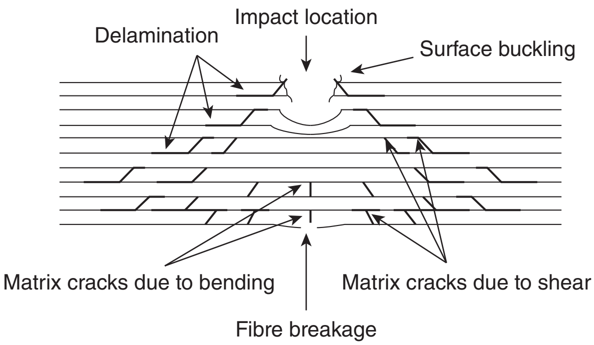
11.3 Phenomenological description of the second phase. *F*, resulted reactive force applied to the composite structure which causes the initiation of matrix cracks or intraply delamination; θ, angle of reactive force *F* with the projectile direction; $\dot{u}_0$, velocity of ceramic plug created at initial impact.



11.4 Ballistic test results for SiC-based ceramic (tile 100 × 100 mm) tested against threats. Caliber 7.62 × 63 mm Armour Piercing (type of rifle) M2 (length of rifle barrel, 10 in).

There is an important parameter that needs to be taken into account when ceramics are used as a strike face namely, the size of the tiles. Indeed, when a tile is impacted, it cracks due to the brittle behaviour of the ceramic. In the case of multiple impacts, if there is only one tile, the first shot will act as described previously, but the others will directly go through and the ceramic will not act efficiently. However, when armours are made with ceramic tiles, more than one tile is set up, in order to limit the propagation of the tile fracture.

In a composite structure, the absorption of energy depends on many parameters such as fibre material, matrix material, fibre/matrix interface, fibre orientation and structural geometry (Guoxing and Tongxi, 2003). As soon as the first layers are impacted, the whole composite structure is stressed (Fig. 11.5) and the energy transfer is governed mainly by the energy



11.5 Schematic representation showing a typical impact damage mode for a composite laminate.

absorption throughout the fibres (Shyr and Pan, 2003). Delamination is induced by the bending of each ply, which causes internal stress due to the difference in the value of the Poisson coefficient of yarns between the plies and the space between them. The effect of cracking along the matrix may be the cause of internal stress. Intra-ply delamination can be caused by the proliferation of matrix cracks (Johnson, 1985). This phenomenon is important in order to achieve energy absorption by ply-to-ply friction in the plane direction (Kang and Kim, 2000).

Taking into account time, three main stresses occur during a ballistic impact (Morye *et al*., 2000):

- the tensile failure of the first yarns,
- the elastic deformation of the structure,
- the intra-laminar ply delamination induced by the projectile.

The duration of each of these three main stresses is directly linked to the projectile velocity and also to the bullet type (shape, compounds, diameter and weight) (Carlucci and Jacobson, 2008).

The behaviour of the bullet varies during impact, depending on its velocity. At 'low' velocity (meaning under about 500 m/s for handgun threats), the bullet will be deformed in a 'mushroom' shape before being stopped. At medium velocity (between 500 and 1000 m/s for rifle ammunitions), the bullet explodes on impact. At very high velocity (above 1000 m/s: IEDs), the target structure acts like a fluid. During impact tests at speeds in excess of 300 m/s, a rigid behaviour of the structure is observed at the beginning of the penetration, causing a fracture in transverse shear of fibres, followed by flexural behaviour, creating multiple delaminations and breaks in tensioned fibres (Vasudev and Mehlman, 1987; Bless and Hartman, 1989; Dorey, 1989; Bannister *et al*., 1998).

The ballistic performance of a flat structure increases with the speed of the 'bending waves' and rupture time of the plies (Ayax, 1993). A

simultaneous increase in these two parameters allows the material to absorb more energy from damage and deformation before the complete rupture of the flat structure. This implies the need to initiate and encourage an early propagation of delamination during the impact in the plate by careful choice of materials. One can, for example, use thick plies having low resistance, to create inter-laminar shear formed by resistant or ductile fibres.

The mechanism of delamination during impact has been the subject of many studies (Ross and Sierakowski, 1973; Cristescu *et al.*, 1975, Sierakowski, 1976). Most authors agree that delamination, along with fibre breakage, is the main mechanism of energy absorption. These mechanisms promote penetration resistance. The thickness of the target needs to be increased in order to improve penetration resistance. An increase in thickness implies an increase in mass per unit area of the composite material (Dorey, 1987; Savage, 1989).

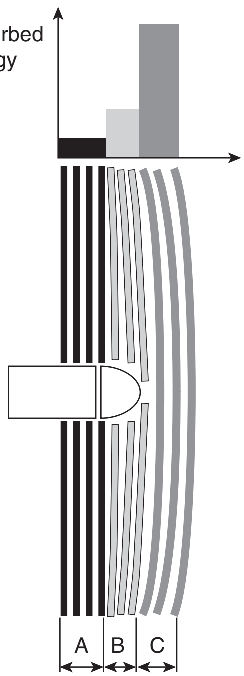
Materials made of ductile fibres (aramid, polyethylene) absorb more energy by deformation in axial compression and are more perforation resistant than materials reinforced with glass fibres (Bathnagar *et al.*, 1990; Hsieh *et al.*, 1990; Cunniff *et al.*, 1989). It can be assumed that there is a joint mechanism, which is governed by the bending rigidity of plies and properties of fibres (which break due to impact). This joint mechanism is responsible for the propagation of delamination and therefore energy absorption in the target plate.

In addition to the components' mechanical properties, the structure and thickness of the fabrics can influence the perforation resistance of a composite plate. In the case of a plate reinforced with aramid fabric, the penetration depth increases with increase of the speed. It therefore appears that the bending rigidity of plies, along with the ply thickness, is crucial to the overall ballistic performance of a plate.

The main energy absorption mechanisms involved in such interactions have been identified (Fig. 11.6). They are:

- transverse shear in broken fibres (Section A),
- tension in broken fibres (Section B),
- delamination (Section C).

There is a competition between the rupture mechanisms of fibres and delamination spread, both of which depend on projectile shape, the characteristics of fracture components and the bending rigidity of plies. Thus, to optimise the impact resistance, we must encourage the spread of delamination, in the sense that the plate has to absorb more energy from damage and deformation of the fibres before the complete failure of the material. Therefore it is necessary to decrease the inter-laminar shear resistance of the material, and increase joint stiffness and the bending plies' resistance to deformation or fibre rupture.

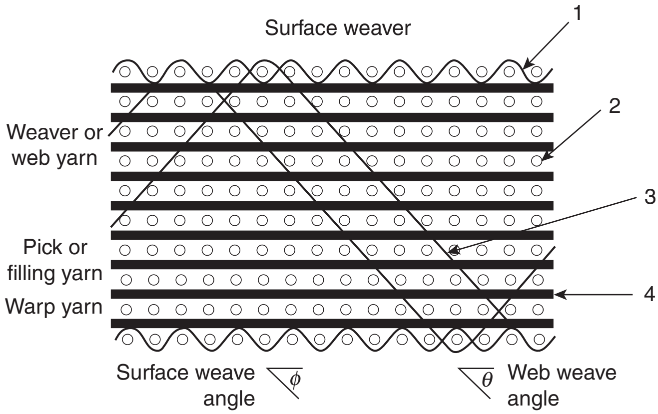


11.6 Explanation of delamination due to ballistic impact. A, transverse shear in broken fibres; B, tension in broken fibres; C, delamination.

The failure mode of orthogonal interlock fabric composites has been examined in detail (Boussu and Begus, 2008). The through-the-thickness yarns tend to increase the energy required to propagate an inter-laminar crack by the mechanism of fracture and pull-out of the z-axis fibres, and crack branching and deviating in the vicinity of z-axis fibres as well as in-plane fibres.

11.3 Bullet-proof textile composites for armoured vehicles

Conventional fabrics are sufficient as existing solutions but cannot help to reduce blunt trauma and weight in soft ballistic protection. On the other hand, for multi-layer fabrics stacked together for use inside an armour-plated solution for hard ballistic protection, low intra-laminar resistance is the main handicap. To cope with this lack of performance, different textile structures are being developed, especially 3D ones such as 3D warp interlock fabrics. Such structures are designed with reinforcement in the thickness direction. This helps in maintaining the cohesion of the structure during an impact and thus reduces the effects caused by intra-ply delamination. Owing to their improved damage tolerance (confining the term to damage



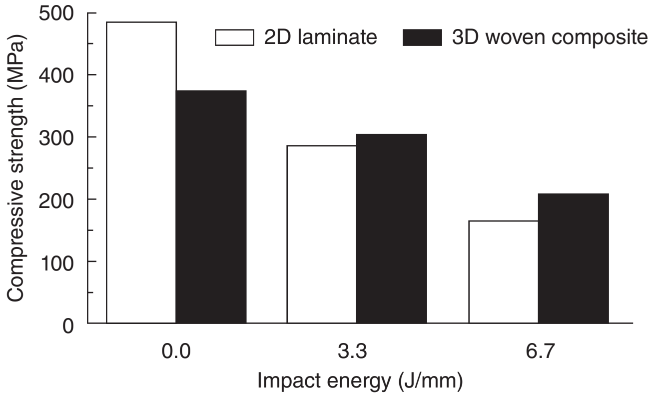
11.7 Schematic representation of warp interlock structure. ϕ, Crimp angle of surface warp yarns (surface weave angle); θ, crimp angle of warp yarns which bind the layers (web weave yarns).

during ballistic impact), warp interlock structures are expected to be more efficient in the case of multiple impacts.

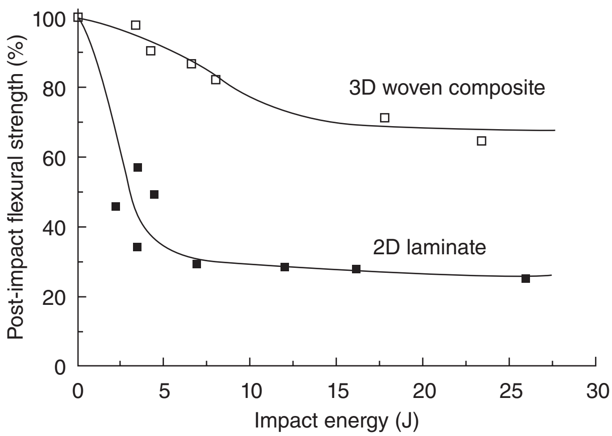
11.3.1 3D-warp interlock fabric as a solution

Figure 11.7 illustrates a 3D warp interlock fabric made of different yarns in the three directions (Hu, 2008). The first yarn (Number 1) called the 'surface weaver', is used when the structure needs a smooth surface and ensures the consolidation of the 3D woven structure from the top to bottom. The second yarn (Number 2) is called the 'fill yarn or weft yarn', and gives the mechanical properties in the transverse direction. The third yarn (Number 3), called the 'warp yarn', is also used for mechanical properties and undergoes undulations because it works in the fabric thickness direction. The fourth yarn (Number 4), called the 'longitudinal yarn' or 'warp yarn', gives resistance and toughness in the longitudinal direction.

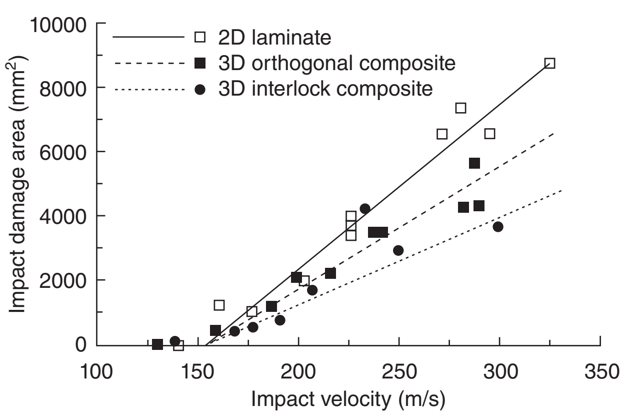
Tong *et al*. (2002) have mentioned that 3D structures show an increase in compression (Fig. 11.8) and flexural (Fig. 11.9) strength, as well as a decrease in the delaminated area (Fig. 11.10) after impact compared with 2D laminates. Moreover, shorter interlacing yarns in some architectures allow fabrics to bend easily and to shear more effectively, unlike with 2D laminates. The main disadvantages encountered with ballistic structures include the adverse effects of crossover points in fabrics and laminate delamination (Dadkhah *et al*., 1995; Chiu *et al*., 2004). This is a significant factor in the case of multiple-impacts because the integrity of the structure is adversely affected. Integrating diverse technologies, including 3D textile fabrics, in order to take advantage of their strong points seems to be the most interesting solution.



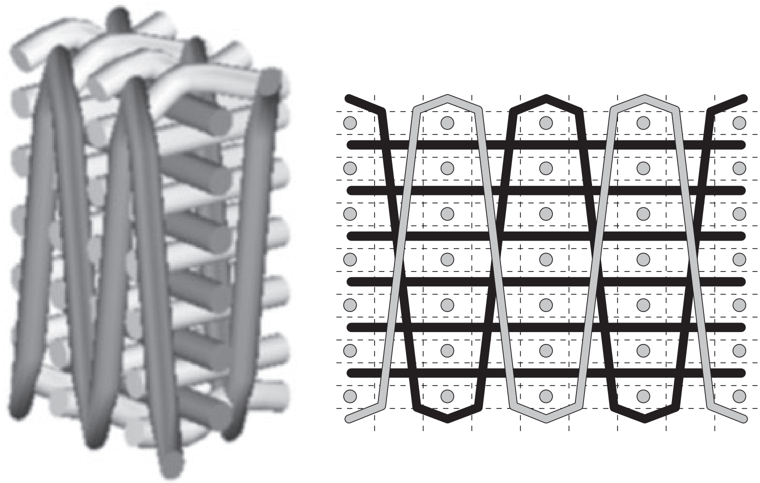
11.8 Effect of weaving on compressive behaviour.



11.9 Effect of weaving on flexural strength.



11.10 Effect of weaving on impact damage area.



11.11 Illustration of an orthogonal warp interlock woven fabric (seven layers). (a) 3D view, (b) warp yarn evolution.

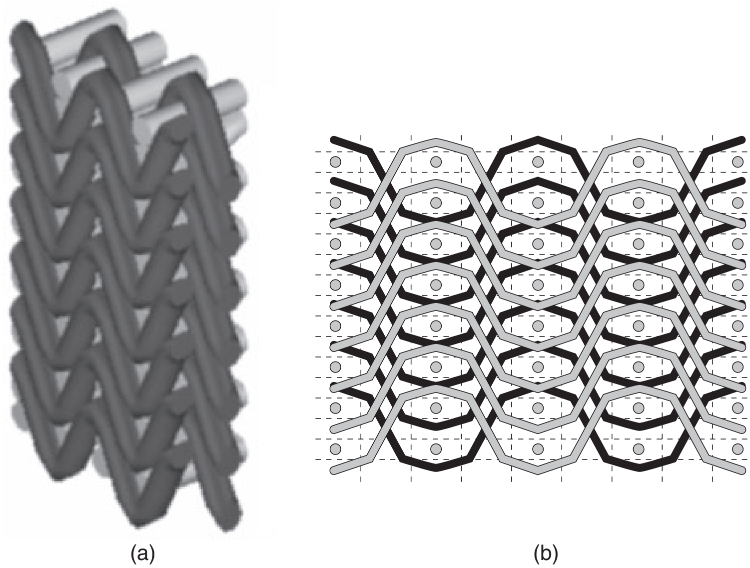
Different types of 3D woven architectures can be chosen. The choice allows one to design composite material having suitable tensile strength, shear strength and delamination properties according to the expected nature of the ballistic impact (Tsai *et al*., 2000; Sun *et al*., 2005, 2009). Three types of multilayer woven architectures, namely layer-to-layer, orthogonal and through-the-thickness interlocks, can be designed within the framework of warp interlocks.

In the orthogonal warp interlock fabrics (Fig. 11.11) (Wisetex® Software), the z-yarns go through the entire thickness of the fabric between only two columns of weft yarns. The main advantage is the presence of the column of longitudinal yarns, which improves the mechanical properties of the fabric and limits the crimp inside the structure. Conversely, the two yarns that go through the thickness induce a weakness zone.

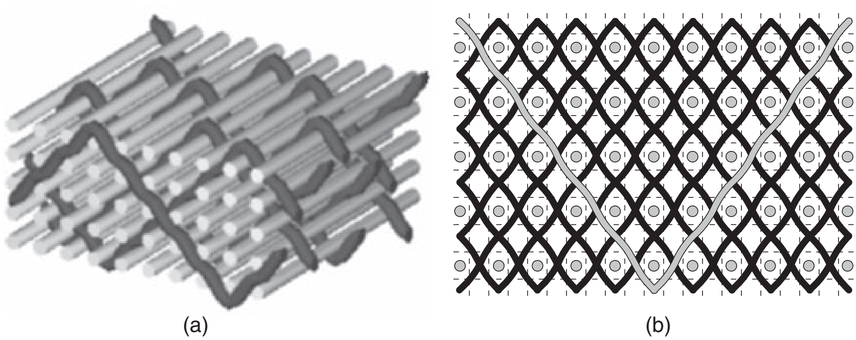
In the layer-to-layer interlock fabrics (Fig. 11.12), the z-yarns connect individual layers of the fabric. This type of architecture allows control of crimp. Indeed there are many configurations and quantities of z-yarns that can be selected in order to assemble the layers together.

In through-the-thickness interlocks (Fig. 11.13), the z-yarns traverse the entire thickness of the fabric across more than two columns of weft yarns. This configuration induces greater thickness than other types. It is possible to introduce a longitudinal yarn inside the structure in order to compensate for the loss of mechanical properties.

In view of the advantages represented by warp interlock fabrics, one of the proposed solutions to improve the ballistic protection for vehicle armour



11.12 Illustration of a layer-to-layer interlock woven fabric (eight layers). (a) 3D view, (b) warp yarn evolution.



11.13 Illustration of a through the thickness interlock woven fabric (five layers). (a) 3D view, (b) warp yarn evolution.

and reduce the weight is to integrate 3D fibrous architectures at different specific locations, allowing the absorption of an estimated amount of energy.

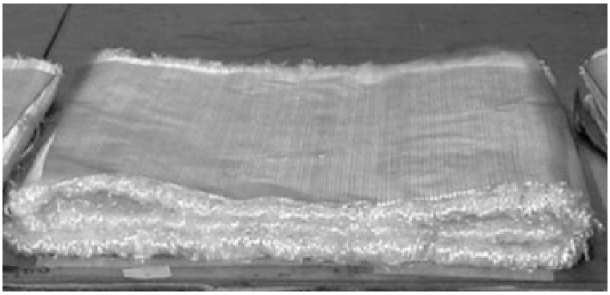
11.3.2 Design of a new armour-plated protection system

The particular advantage of ceramic backed by composite armour lies in its high hardness and relatively low density as compared with steel plates (for similar energy absorption) (Boussu and Begus, 2008). As soon as an

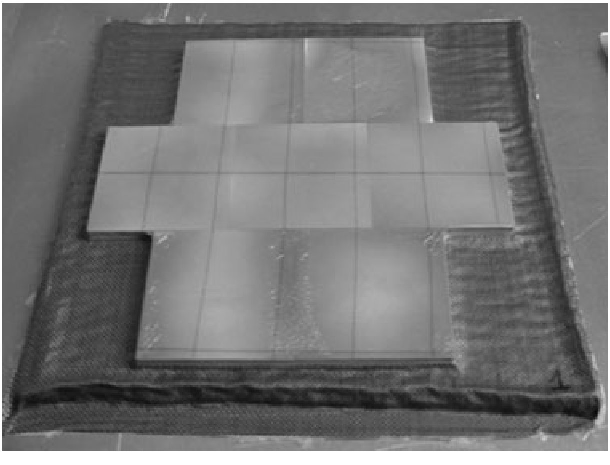
armour-piercing bullet impacts the hard armour, the ceramic strike face deforms and breaks up the bullet, thereby greatly decreasing the impact energy. Then, the backing, located behind the ceramic plate, absorbs the energy by deforming the fibrous structure and thus stops the fragments.

The ceramic facing-element can be a continuous monolithic plate or a plurality of individual square ceramic tiles or otherwise, and can be shaped to suit the dimensional needs of a particular application. The most used ceramic types are alumina Al_2O_3 (ρ = 3.9 g/cm^3), silicon carbide SiC (ρ = 3.2 g/cm^3) and boron carbide B_4C (ρ = 2.52 g/cm^3). Different layers of the textile structure are stacked together to achieve the final backing of the target (Fig. 11.14). Ceramic tiles or alumina ones are placed in front of the textile structure to be moulded and pressed during the composite manufacturing process (Fig. 11.15).

Three targets have been tested with 12.7 mm calibre armour piercing ammunition of 43 g weight, which corresponds to a total energy of around



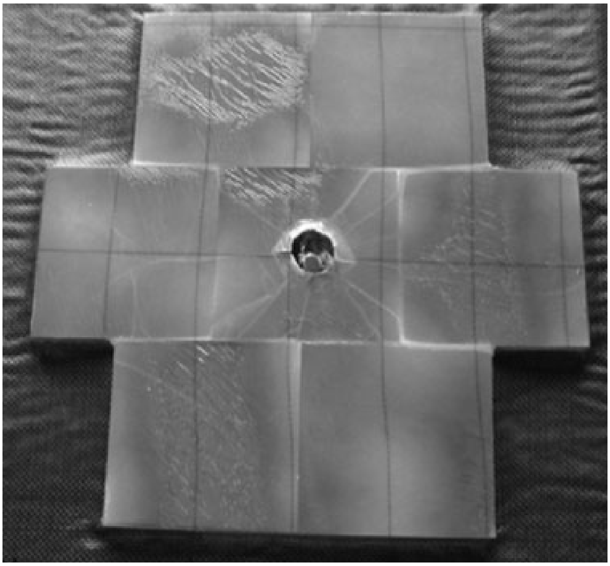
11.14 Stacking of three layers of angle interlock fabric.



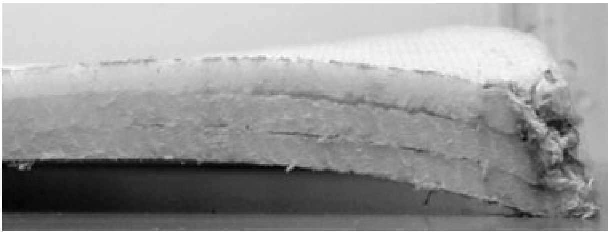
11.15 Final view of the target.

8000 J to be absorbed. Only one bullet was fired, at the centre of each target with a speed of 610 m/s, in accordance with the MIL-PRF-46103-E standard (for use in the field of aeronautics only). None of the targets failed during impact tests. For one of the targets, the impact hole had a diameter of 25 mm. After the first impact (Fig. 11.16), most of the ceramic tiles were still 'glued' to the backing, which may have led to better propagation of kinetic energy to the textile backing.

Post mortem analysis (Fig. 11.17) of the 3D woven textile composite removed from the target allowed a better understanding of its ballistic performance. It was revealed that intra-ply delamination between the three 3D warp interlock fabrics leads to better energy absorption during the impact of deformed hard core ammunition. This target made with warp angle interlock fabric was compared with existing unidirectional laminates.



11.16 Impacted target with 12.7 mm cartridge.



11.17 Lateral view of the 3D textile composite of the final target.

It was found that the same bullet-stopping result is achieved for both the targets, but the cost of production for warp angle interlock fabric is reduced by half, along with a 10% weight reduction. This is primarily due to the good delamination resistance of the 3D woven fabric and one-step production made possible by the 3D interlock weaving process.

In conclusion, a 3D warp interlock fabric used as the reinforcing fibrous material inside a textile composite stacked with ceramic tiles allows reduction of mass, with the same ballistic protection for vehicle armouring. The predicted behaviour of these three warp interlock fabrics during the impact corresponded well with their actual behaviour. In order to improve the performance of this protection under identical firing conditions, a localised measurement of energy dissipation inside the warp interlock fabric would help to better understand the mechanical stresses and their spread under dynamic conditions. Thus, the other part of our research is related to the development of sensor yarns for real time *in-situ* measurement of stresses acting on the target during an impact. The mechanical properties of yarns vary greatly during an impact, depending on the impact velocity. That is why, initially, our research focused mainly on real time, *in-situ* monitoring of quasi-static tensile loading using flexible textile sensors.

11.4 Using sensor networks in composites to measure impact behaviour and material performance *in situ*

Good quality and reliability are basic requirements for advanced composite structures, which are often used under harsh conditions. To improve their performance, monitoring during the curing process is clearly necessary. At the same time, in service, non-destructive evaluation (NDE) is needed to keep these structures operating safely and reliably. NDE techniques have been developed in the past, including ultrasonic scanning, acoustic emission (AE), shearography, stimulated infrared thermography (SIT), Fibre Bragg Grating (FBG) sensing and vibration testing (Black, 2008).

The challenge today is to develop new, low-cost techniques that can perform online structural health assessment, starting from the manufacture of composite structure to the actual service of these structures in the field. Moreover, NDE techniques have to be integrated in the design phase, and sensors should be inserted during the fabrication of composites in order to improve accuracy and reduce costs. The classical NDE techniques are difficult to adapt. They are not well suited for on-line structural health monitoring because of difficulties in making *in-situ* implementation. Moreover, it is important to understand the stress–strain conditions during damage. A record of stress–strain history prior to damage also helps in understanding the cause of irreversible damage (Wang and Chung, 2006).

One possible solution is to use intelligent textile materials and structures that provide a real possibility for on line and *in-situ* monitoring of structural integrity. These materials not only perform the traditional functions of a structural material, but also have actuating, sensing and microprocessing capabilities. Such intelligent materials are made by coating or treating textile yarns, filaments or fabrics with nanoparticles or conductive and semi-conductive polymers, giving them special properties (Scilingo *et al.*, 2003; Dharap *et al.*, 2004; Fiedler *et al.*, 2004; Lorussi *et al.*, 2005; Huang *et al.*, 2008a, b).

A review of piezoresistive sensing approaches already being applied to measure strain in fabrics/composites shows that several sensing mechanisms exist. These approaches may be categorised, on the basis of manufacturing technology, as follows.

- Nanotube networks (Zhang *et al.*, 2006; Schueler *et al.*, 2001; Fiedler *et al.*, 2004; Peng *et al.*, 2001).
- Carbon tows for self-sensing (Wang and Chung, 2006).
- Semi conductive coatings (Dharap *et al.*, 2004; Cochrane *et al.*, 2007; Peng *et al.*, 2001).

None of these have gained universal acceptance, either as standards in structural health monitoring of composites or for the fabrication of intelligent textiles.

Nanotubes have been investigated in detail for use as sensing mechanisms, both for smart textile applications and for structural-health monitoring of composites. Significant challenges still exist in their development; for example, the efficient growth of macroscopic-length carbon nanotubes, controlled growth of nanotubes on desired substrates, durability of nanotube-based sensors and actuators, and effective dispersion in polymer matrices and their orientation. Therefore, there is a need to develop both experimental and analytical techniques to bridge the nano and macro scales towards optimization, so as to use nanotube networks as sensors inside macro-scale (fabric) or meso-scale (tow) composites (Lorussi *et al.*, 2004).

Carbon-fibre reinforced composites offer a unique possibility of using carbon tows as a sensing network because of their conductivity. However such an approach can only be used for conductive fibre based composites. Moreover, before applying such an approach for structural health monitoring it is imperative to understand the deformation mechanism of the reinforcement. Any anomaly in the deformation mechanism can threaten the sensing mechanism's validity and efficacy.

Semi-conductive coatings, such as silicon flexible skins, have been used for intelligent textiles (Katragadda and Xu, 2008), e.g. as flexible fibrous transistors (Fiedler *et al.*, 2004; Lee and Subramanian, 2005) on textile fibres, to detect the physiological condition of the wearer (Huang *et al.*, 2008a, b;

Scilingo *et al*., 2003; Cochrane *et al*., 2007). Such coatings on fabrics, yarns or fibres are easy to realise and can be made wash resistant. Their use as electrical percolation networks for sensing in structural-health monitoring applications is quite promising and needs to be further investigated. Electrical percolation is a phenomenon defining the transition from an electrically non-conductive to an electrically conductive state of the sensor. Conductive paths constituted of conductive particles (charges) contributing to percolation appear when the strain gauge length decreases (global sensor resistance decreases) and disappear when its length increases (global sensor resistance increases). Therefore, the global sensor resistance used to measure the elongation of the sensor depends on the number of electrically conductive paths. This type of sensor is also called a piezoresistive sensor.

New piezoresistive textile sensors based on semi-conductive coatings has been designed, developed and optimised by GEMTEX Laboratory (France). They are suitable for use in composite structural parts reinforced with 3D preforms and have been specially designed to offer the following advantages.

- They can be embedded inside the reinforcement during weaving.
- They have all the characteristics of a traditional textile material (light weight and flexibility, and thus the capability to adopt the geometry of the reinforcement and become an integral part of it).
- Since these sensors are inserted during the weaving process, they are subjected to similar strains as the composite itself. Measurement of resistance change with variation in the sensor's length is a way of determining, *in-situ*, strains in the composite material that lead to its final damage.
- The fibrous sensors are not supposed to modify the overall structural and mechanical properties of the composite as they are integrated locally and the bulk of the structure is composed of high-performance multifilament tows.
- Embedding such an intelligent piezoresistive sensor inside the reinforcement during the weaving process is the most convenient and cost-effective way of inserting a sensor for structural health monitoring (SHM).

Development and optimisation of such piezoresistive sensors has been carried out in order to render them sensitive enough to measure *in-situ* strains inside the composite part. Sensitivity is important as the targeted application usually undergoes very low strains, but even such low strains and/or vibrations during the life-time of composite parts are critical. Often they are used in areas where structural integrity cannot be compromised (aircraft wings, bodies, etc.). Optimisation of sensors is followed by their insertion in the reinforcement, during the weaving process, on a special

loom modified and adapted for multilayer warp interlock weaving. The reinforcement is then impregnated with epoxy resin, using an infusion process, to form a stiff composite material.

In the first place, only tensile loading was considered in order to validate the concept of *in situ* measurement with the sensor, compatible with the manufacturing method of carbon composites. Afterwards, fatigue and impact monitoring using the same kind of sensors will be realised. The fatigue properties may also be estimated from the history recorded during the target's life time using our fibrous sensor.

Since the carbon multifilament tows are conductive and may disturb the functioning of the piezoresistive fibrous sensor, it is imperative to coat the sensor with an additional insulating layer. The compatibility of the interfacial properties of the insulating layer with the carbon nanoparticles coated on the sensory yarn surface on one side and with the epoxy resin on the other side is very important. An insulating medium that has good adhesion to the coated yarn, as well as with the resin, should be used.

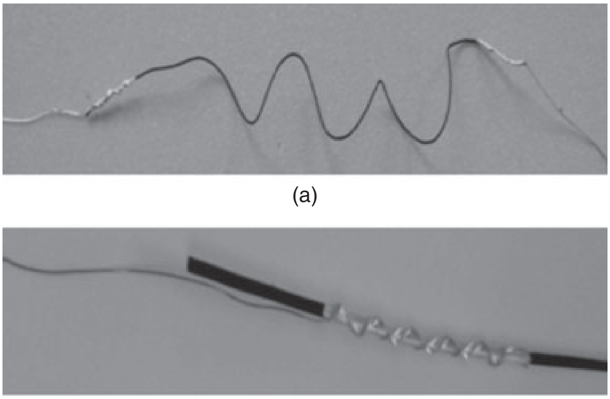
11.4.1 Sensor design

Several different coating techniques for intelligent textile structures exist. The one described here was developed by Cochrane *et al*. Yarns and filaments were coated with the conductive layer using dispersed carbon black particles (Printex® L6) in polymer (Evoprene® 007) solution, utilising chloroform as a solvent and dispersing medium. In order to characterise the sensitivity and adherence of the coating on different substrates, a solution having 35% carbon black concentration was coated onto various yarns and filaments (polyester, polyamide, polyethylene and cotton). It was found that polyethylene was the best substrate as far as resistivity and uniformity of the conductive layer was concerned. The coatings on polyethylene were easy to achieve due to good substrate–conductive solution interfacial properties. Coatings on polyethylene were reproducible and gave coherent results. Therefore two-ply polyethylene filament was chosen for sensor development.

The fundamental principle of functioning of this fibrous strain gauge is based on forming (and deforming) the electrical conductive paths (percolation networks) in a coated layer made of conductive nano charges with gauge deformations. Sensor structural and geometrical parameters, along with initial electrical resistance, are shown in Table 11.1. The two ends of the coated polyethylene filaments were additionally coated with silver paint, and fine copper wire was attached to the two ends with the help of this paint (as shown in the Fig. 11.18). In this way, secure connections were realised, enabling the reduction of the contact resistance to a minimum. Transversal and longitudinal sections of the sensor, obtained through SEM

Table 11.1 Sensor properties

Parameter	Value
Linear density of the filament	48.23 g/km
Diameter of the filament	0.70 mm
Average width of the sensor	1.68 mm
Average thickness of the sensor	1.26 mm
Aspect ratio of the sensor	1.33
Initial resistance of the sensor	43.30 kΩ



(a)

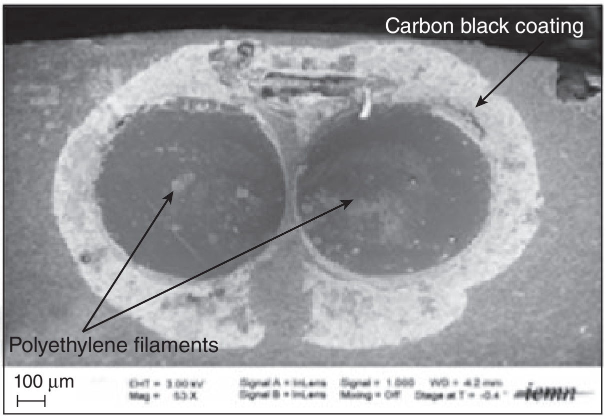
(b)

11.18 Textile sensor before its integration in woven fabric. (a) Carbon black-coated sensor with polyethylene double-ply substrate, (b) detail of connections at the ends.

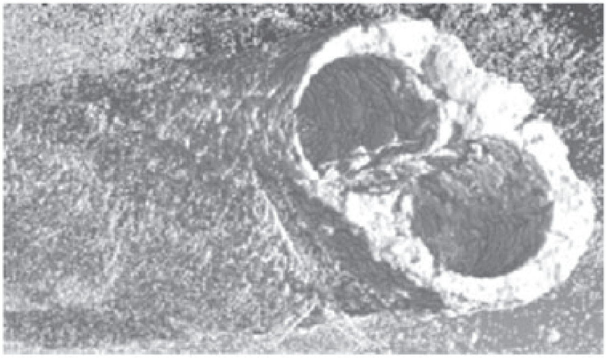
and tomography, are shown in Fig. 11.19a and 11.19b, respectively. For insertion in conductive, fibre-based reinforcements, such as that woven using carbon multifilament tows, the sensor was coated with Latex Abformmasse supplied by VossChemie®, so as to insulate the sensor from the surrounding carbon tows.

11.4.2 Reinforcement architecture and sensor insertion

An orthogonal/layer-to-layer interlock structure with 13 layers was woven on a modified conventional loom. 200-tex multifilament carbon tows (6K), supplied by Hercules Inc., were used in the warp and weft. The reinforcement and composite parameters are listed in Table 11.2. Sensors can be inserted in warp or weft directions during weaving. Given the technical complications associated with sensor insertion in the warp direction during weaving on a loom, insertion in the weft direction has been carried out for



(a)

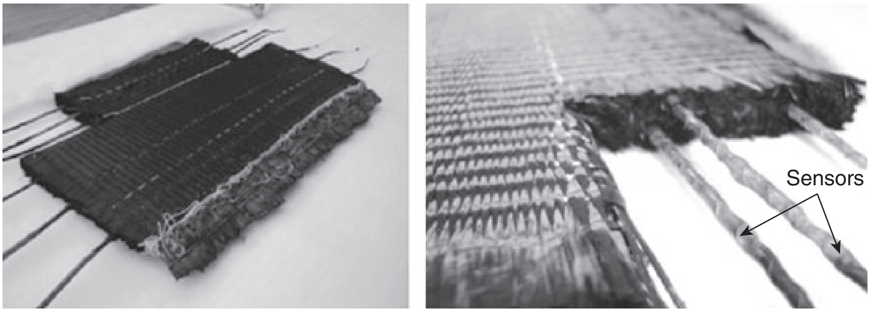


(b)

11.19 Images of the sensor obtained through SEM and tomography. (a) Transversal section (SEM), (b) longitudinal view (tomography).

Table 11.2 Reinforcement and composite specifications

Parameter	Value
Linear density of warp tow	200 g/km
Linear density of weft tow	200 g/km
Average thickness of reinforcement	6.5 mm
Warp tows density	24 tows/cm
Weft tows density	169 tows/cm
Areal weight	3908 g/m^2
Fibre volume fraction	34.16%



11.20 Reinforcement with protruding sensor connections.

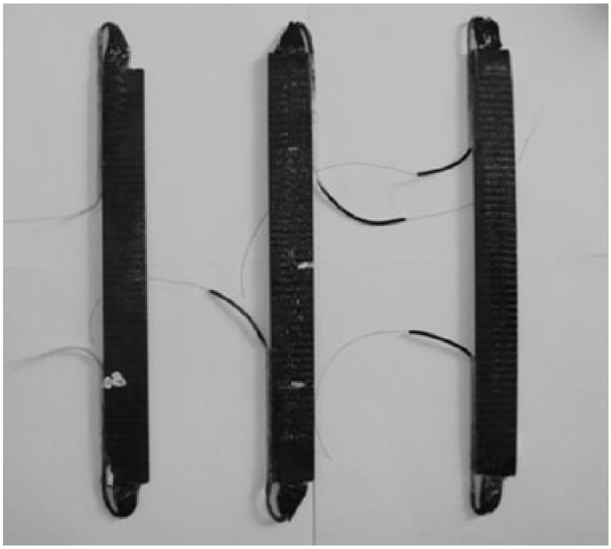
preliminary studies. The location of the sensor in the reinforcement was chosen to be in the middle of the structure. Moreover, since the sensor is inserted during the weaving process, it follows the same trajectory as the carbon tows inside the reinforcement. Figure 11.20 is a photograph of the off-the-loom dry reinforcement. Latex-coated sensor connections can be seen protruding from the reinforcement.

11.4.3 Composite manufacturing process

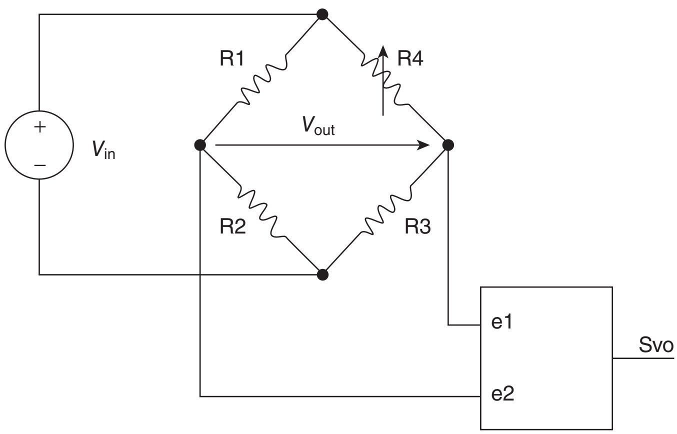
After weaving, the reinforcement was carefully removed from the loom and was impregnated using a vacuum bag infusion process in order to make the composite part stiff. The resin employed was epoxy Epolam 5015. The two connections of the sensor that remained outside the reinforcement at the two ends were carefully separated from the rest of the mould. This was done by creating two vacuum sub-moulds inside the larger mould so that the resin could not impregnate the two connections of the sensor. The impregnated composite samples were cut into slabs of 25 cm × 2.5 cm (Fig. 11.21).

11.4.4 Preliminary sensor measurements (before insertion in composite)

The sensor was tested in traction on an MTS ½ tester (MTS, Material Testing System). The sensor underwent quasi-static tensile loading at a constant test speed of 5 mm/min. A Keithley® KUSB-3100 data acquisition module was employed for the purpose of determining voltage variation during data acquisition. A Wheatstone Bridge (Fig. 11.22) was used to measure the unknown variable resistance of the sensor as a function of output voltage. The data acquisition module, when connected to a computer, showed the voltage variation data in real time via the software interface (Keithley QuickDAQ). The data could be saved on a hard disk for further



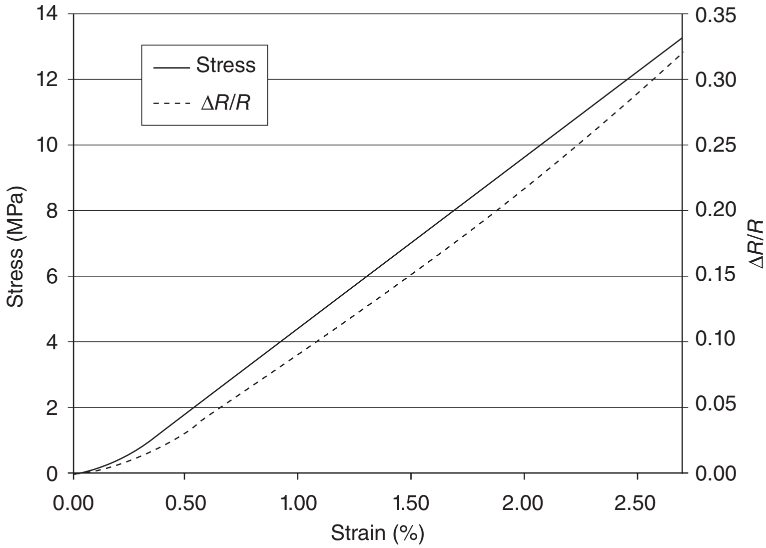
11.21 Composite structural part with textile sensor for tensile test.



11.22 Wheatstone bridge configuration used for differential voltage variation measurement caused by resistance variation in the sensor R4 (strain gage). R1, R2, R3 are resistors; V_{in}, input or excitation voltage; V_{out}, output voltage; e1 and e2, analog to digital converter input; Svo, signal to computer.

treatment in any suitable format. Noise reduction in the resistance variation data was achieved using a low pass filter.

The resultant stress–strain–resistance relationship curve, up to 2.5% elongation of the out of composite sensor (before insertion in the reinforcement), is shown in Fig. 11.23. It may be noticed that the stress *vs.* strain curve has the same shape as the normalized resistance ($\Delta R/R$) *vs.* strain



11.23 Normalised resistance, and stress against strain for sensor outside composite.

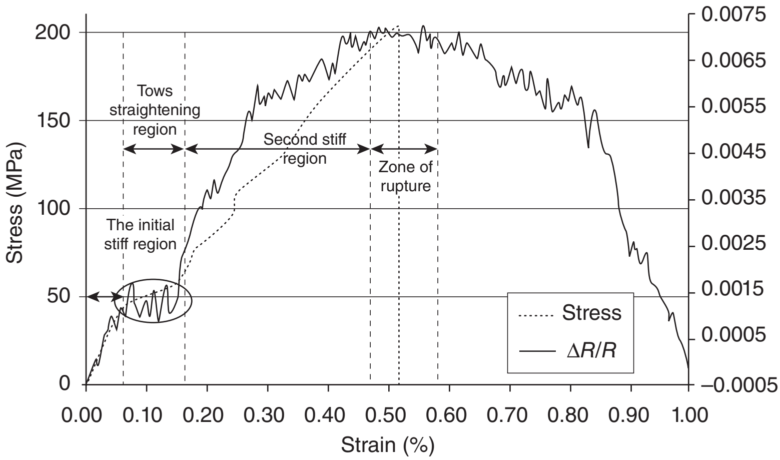
curve. This validates the electromechanical properties of the fibrous sensor for strains ranging from 0 to 2.5%.

11.4.5 On-line sensor measurements (after insertion in composite)

The composite specimens were tested on an Instron© 8500 tester (Fig. 11.24). Tensile strength tests were performed on the composite specimens according to the standard NF EN ISO 527–4, 1992, in the weft direction, i.e. the direction parallel to the inserted sensor. The same Wheatstone bridge was used for resistance variation measurement and the configuration of the testing equipment was also kept the same. The composite structural part was tested at a constant test speed of 5 mm/min. The composite underwent traction until rupture.

The resultant stress–strain–resistance relationship curve is shown in Fig. 11.25. It can be seen that the normalised resistance follows the stress–strain curve. The stress–strain–resistance curve can be divided into four regions, namely: the initial stiff region where the composite exhibits toughness against the applied load represented by a high slope, a second region called the ‘tows straightening region’. It is followed by another stiff region, and finally the zone of rupture. The rupture occurred at the strain of 0.52%, after which the tensile strength tester came back to its initial position at the same speed (5 mm/min.). Since the fibrous sensor had not been broken,

11.24 Instron 8500 tensile strength tester.



11.25 Normalised resistance and stress against strain for sensor inside composite.

ΔR/R decreased until zero as the tester returned to its initial position. However this decrease was not linear because the sensor was still intact while the resin–sensor interface was partially damaged, causing its non-linear behaviour.

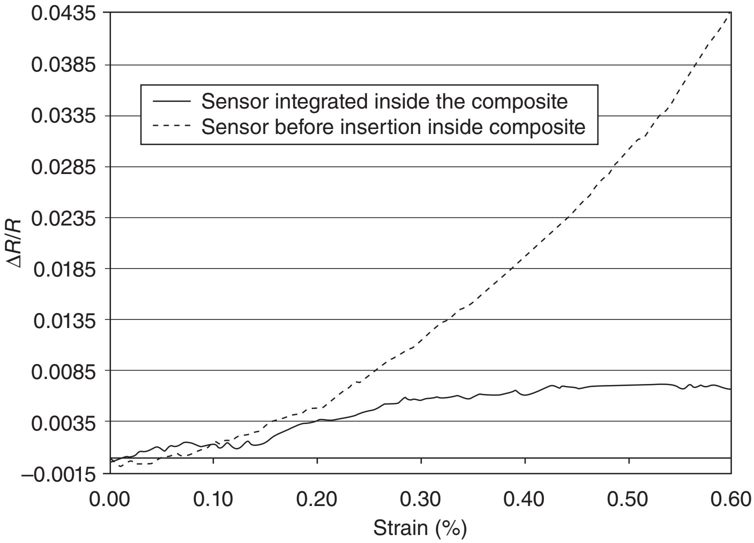
A composite micrograph in the weft direction revealed that the weft tows were highly crimped. In the initial stiff region, micro-cracks start appearing

as the composite specimen undergoes traction, but the interface between resin and multifilament tows is still intact. That is why the composite exhibits rigid behaviour. In Fig. 11.25 it can be observed that, after the initial stiff region, the highly crimped tows tend to straighten due to increasing tensile load in the second region. In this region, the micro-cracks give way to relative slippage of the highly crimped tows in the matrix, i.e. the resin–tow interface is relatively weakened. This region, called the tow straightening region, is enclosed in an ellipse in Fig. 11.25. The region is characterised by high Poisson contraction. It can also be remarked that the sensor resistance follows the stress–strain curve, but in the second region, the electrical resistance curve is noisier as compared to other regions of the curve, which might signify slippage of the tows, as well as the sensor, in their sockets.

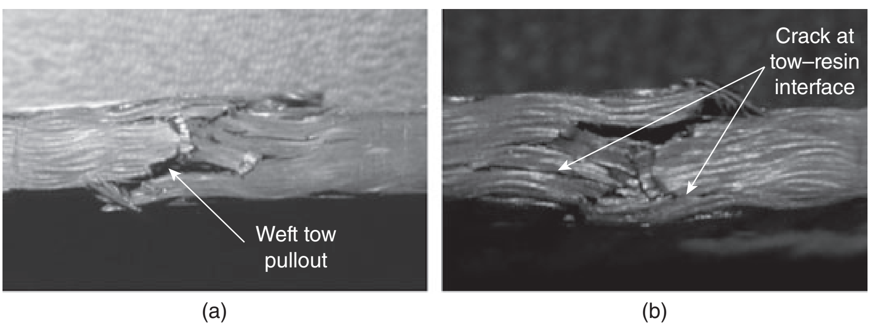
This second region is followed by the third region called the 'second stiff region' where the tows are locked in their sockets. In this region the tows resist the applied load and exhibit stiff behaviour as they regain some of their initial stiffness after the straightening of tows in the second region. The electrical resistance varies almost linearly with the applied load in this region. The third region is followed by the zone of rupture of the composite, in which the electrical resistance, having attained the highest value, starts dropping down. The normalised resistance starts dropping after the rupture. The fact that the sensor resistance attains its initial value after the rupture signifies that the sensor, owing to its elastic properties, is not destroyed with the composite.

In Fig. 11.26, a comparison of the electrical resistance variation of identical out-of-composite and *in-situ* sensors is given. Initially, the sensors behave essentially in the same way, as is obvious from the two curves. The two curves part ways at around 0.20% elongation, which roughly coincides with the beginning of the third region, namely the second stiff region in Fig. 11.25. Unlike the *in-situ* sensor, the out-of-composite sensor has linear resistance–strain relationship. This difference in the two curves signifies the differences in the region around the two sensors. The out-of-composite sensor is unconstrained while the *in-situ* sensor is constrained by the reinforcement and resin inside the composite as it has to follow the deformation pattern of the composite.

In Fig. 11.27, photographs of specimens that have undergone these tensile tests are shown. The mode of rupture for all the samples was nearly the same. There was a single zone of rupture half way along the length of samples where tows give in to applied traction in rather a brittle fashion. Tow pull out could also be seen in some of the samples but did not seem to be the dominant mode of rupture (Fig. 11.27a). Low strain to failure was due to low fibre pullout during failure. The initial crack seems to have rendered the structure weak. The crack then propagated in the structure until the complete fracture of tows at the zone of rupture (Fig. 11.27b).

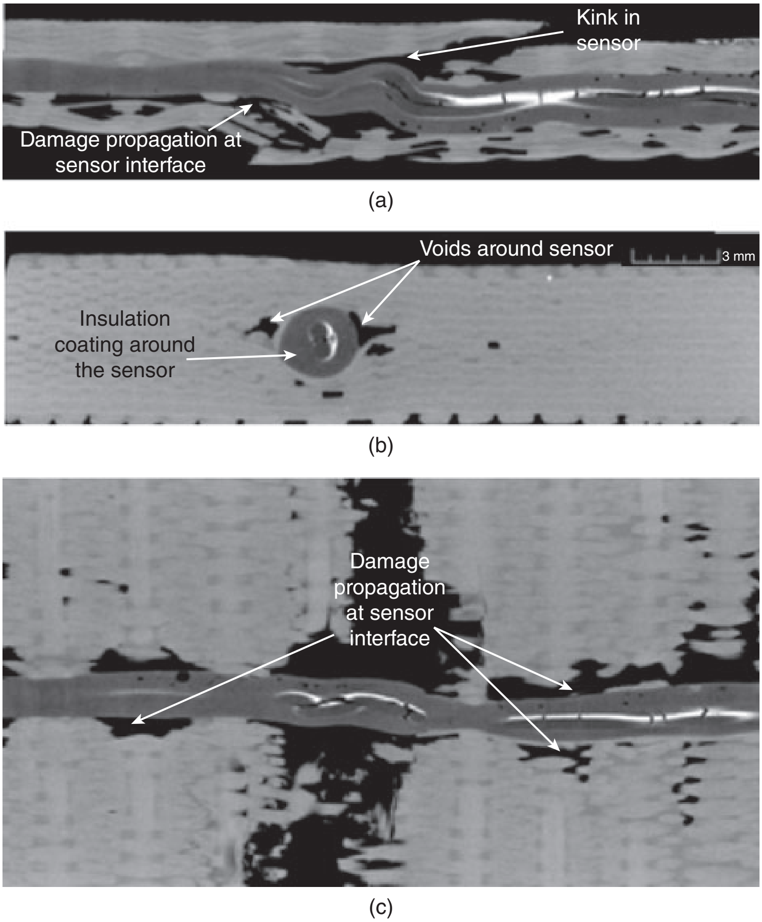


11.26 Normalised resistance against strain for integrated and out-of-composite sensors.



11.27 Surface photographs of composite samples taken after tensile strength tests. (a) Warp tow pullout, (b) crack at tow–resin interface.

Figure 11.28 shows tomographical images of the samples that underwent traction. The sensor cross-section and its path at and near the zone of rupture can be observed. In Fig. 11.28(a, b, c), it can be observed that the sensor–resin interface had many voids. These were caused by poor resin–sensor interfacial properties. The insulating medium on the sensor surface needs to have good adherence with the epoxy resin and carbon fibre reinforcements. Damage that occurred at the main rupture zone had propagated along the sensor boundary, giving rise to debonding of the sensor. A kink in the sensor can be observed (Fig. 11.28a) which was caused by the relaxation of the sensor as it tried to regain its original dimensions after the



11.28 Tomographical images of sensor inside a tested sample near the zone of rupture. (a) Longitudinal section, (b) transversal section, (c) top view.

tensile loading damaged the composite sample. The insulation coating around the sensor rendered it thick, which is undesirable for high-performance composite materials because thick insulation coatings might adversely affect the mechanical properties.

In conclusion, the sensor developed for *in-situ* measurements on carbon fibre composite structures is capable of detecting strain in the structure. The electrical resistance variation in the sensor follows the deformation pattern of the composite, mainly due to its sensitivity to its environment and because of the fact that it is integrated in the structure and follows the fibre architecture of the reinforcement. It has been shown that integrated textile sensors inside the reinforcement can be used as *in-situ* strain gauges for composite materials. Moreover, if the placement of these sensors inside the

reinforcement is carefully chosen, they can be used to follow the local deformation pattern so as to better understand the deformation mechanisms and predict the life-time of the composite parts. At present, the sensors have been tested for tensile loading. Tensile strength tests were chosen to demonstrate the basic features of this novel SHM approach. In the future, these sensors will be used for bending and fatigue tests on similar 3D carbon fibre woven reinforcement-based composites.

However, optimisation of sensors needs to be carried out in order to prepare thinner sensors having negligible effect on reinforcement geometrical and mechanical properties. For carbon fibre based reinforcements, which require an insulation coating on the sensor surface, a better and finer coating needs to be applied. In view of the test results presented, it can be concluded that these sensors can be used for *in-situ* health monitoring of various types of composites under quasi-static mechanical stress, especially for different deformation modes of 3D or multilayer reinforcements in which different layers do not necessarily deform in a homogenous manner. For instance, the fibrous sensors may well be used for the detection of transverse strains and for the detection of interlaminar slippage.

Currently, research work is being carried out in our laboratory to develop sensor yarns suitable for detecting dynamic loads and ballistic impacts. The main challenge lies in the development of a highly sensitive sensor, and a data acquisition and treatment module capable of detecting high-speed ballistic impacts properly and accurately. It is expected that such intelligent systems for ballistic impacts will soon be developed and optimised in our laboratory thanks to our already developed expertise in the field of quasi-static tensile stress monitoring using flexible textile sensors.

11.5 Conclusion

A new textile composite solution, made as part of a final target, was found to resist ballistic impact well. This result was mainly due to the introduction of 3D warp interlock fabrics, stacked together with ceramic tiles to absorb the energy during the impact of 12.7 mm armour piercing ammunition at a speed of 610 m/s. A new sensor yarn, introduced in a 3D warp interlock, has been developed for on-line monitoring of quasi-static tensile stresses. The fibrous sensor yarn is able to detect strain in the composite part and thus acts as an *in-situ* strain gauge. This important innovation will lead some way towards the development of intelligent textile sensors and related data acquisition modules for real time *in-situ* monitoring of energy dissipation in composites for armoured plating. It is expected that these innovations and their integration for the development of intelligent armoured solutions will help us better understand the real behaviour of the final target. The next step in our research thus constitutes the development of sensors

capable of detecting high-speed ballistic impacts when embedded inside armoured plating.

11.6 Future trends

Intelligent textiles for armoured vehicles could be widely used in the future to better protect and adapt the armouring against not only conventional and NATO certified ammunitions, but also against non-conventional weapons such as IEDs. The armouring shape of the vehicle could be made auto-adaptable so as to change the form of the vehicle when faced with threats detected immediately by sensor yarns. In this way, mechanical stress and energy absorption could be actively managed during the impact. This could lead to better use of different active and passive materials, combined in the armour to resist against different types of ballistic impacts.

Structure modifications can be observed during the impact, using an auto-adaptive material such as a shape memory alloy. This has the capacity to change from a martensitic to an austenitic phase under different ambient conditions (including temperature and mechanical stress). The main difficulty lies in the capacity of these materials to be effective against high-speed impacts and their ability to react within a suitable time frame.

Maintenance of vehicle armour could be facilitated by the use of *in-situ* sensor yarns, as these yarns can detect damaged zones and the extent of the damage. This could help minimise down time, reduce maintenance costs and avoid undue loss of personnel and material in the battle field. Another interesting feature that could be developed in the future for better protection of vehicles in a battle field includes the ability to immediately change colour using active chemical agents or reproduced 'biological molecules' (as contained in octopus skin), driven by high-speed electric pulses generated by sensor yarns. This perspective helps firstly to adapt the colour of the vehicle in the human visible range to its environment and secondly to spread the signal detection to UV or IR frequencies. Active camouflage solutions could be developed through the use of sensor yarns.

11.7 References

ACARE (2008). *Addendum to the Strategic Research Agenda*. Available from: http://www.acare4europe.com/

Ayax E (1993). *Caractérisations expérimentales et modélisation du comportement d'une plaque composite tissée en regime balistique*, thèse de doctorat, Ecole Nationale Supérieure D'arts et Métiers, Paris, FRANCE, 19th July.

Bahei-El-Din YA and Zikry MA (2003). Impact-induced deformation fields in 2D and 3D woven composites, *Composite Science and Technology*, 63, 2003, 923–942.

Bannister MK, Callus P, Nicolaidis A and Hetzberg I (1998). The effect of weave architecture on the impact performance of 3D woven composites, *TexComp Fourth International Symposium for Textile Composites*, Japan, 21–7.

Baozhong S, Bohong G and Xin D (2005). Compressive behavior of 3-D angle-interlock woven fabric composites at various strain rates, *Polymer Testing*, 24, 447–454.

Bathnagar A, Lin LC, Chang HW (1990). Ballistic energy absorption of composites, *22nd International SAMPE Technical Conference*, 1–13.

Baucom J and Zikry M (2005). Low-velocity impact damage progression in woven E-glass composite systems, *Composite: Part A*, 36, 658–664.

Black S (2008). Structural health monitoring: composites get smart, *High-performance Composites*. Available from: http://www.compositesworld.com/articles/structural-health-monitoring-composites-get-smart.aspx

Bless SJ and Hartman DR (1989). Ballistic penetration of S-2 glass laminates, *SAMPE Technical Conference*, September, 852–866.

Boussu F and Begus V (2008). *Method of Manufacturing a Composite, Especially a Bulletproof Composite, and Composite Obtained*, Patent WO 2008/152337 A1, GEMTEX Laboratory.

Carlucci DE and Jacobson SS (2008). *Ballistics Theory and Design of Guns and Ammunition*, Taylor & Francis, ISBN-13: 978-1-4200-6618-0.

Chin CH, Lai MH and Wu CM (2004). Compression failure mechanisms of 3-D angle interlock woven composites subjected to low energy impact, *Polymers and Polymer Composites*, 12, 4, 309–320.

Chou S, Chen HC and Chen HE (1992a). Effect of weave structure on mechanical fracture behavior of three-dimensional carbon fiber fabric reinforced epoxy resin composites, *Composite Science and Technology*, 45, 23–35.

Chou S, Chen H-C and Wu C-C (1992b). BMI resin composites reinforced with 3D carbon-fibre fabrics, *Composite Science and Technology*, 43, 117–128.

Chou TW and Ko FK (1989). *Textile Structural Composites*, Elsevier Science.

Cochrane C, Koncar V, Lewandowski M, and Dufour C (2007). Design and development of a flexible strain sensor for textile structures based on a conductive polymer composite, *Sensors and Actuators A*, 7, 473–492.

Cristescu N, Malvern LE and Sierakowski RL (1975). Failure mechanisms in composite plates impacted by blunt-ended penetrators. Foreign object impact damage to composites, *ASTM STP 568*, 159–172, 1975.

Cunniff PM, Song JW and Ward JE (1989). Investigation of high performance fibers for ballistic impact resistance, *21st International SAMPE Technical Conference*, September 25–28, 840–847.

Dadkhah MS, Cox BN and Morris WL (1995). Compression-compression fatigue of 3D woven composites, *Acta Metallurgica et Materiala*, 43, 12, 4235–4245.

Dharap P, Zhiling L, Nagarajaiah S and Barrera EV (2004). Nanotube film based on single-wall carbon nanotubes for strain sensing, *Nanotechnology*, 15, 379–382.

Dorey G (1987). Fracture of composite and damages tolerance, *Agards Lecture Series No. 124*.

Dorey G (1989). An overview of impact damage in composites, *International Conference or Mechanical Properties of Materials at High Rates of Strain*, Conference Series–Institute of Physics, ISSN 0305-2346, 395–402.

Feli S and Asgari MR (2011). Finite element simulation of ceramic/composite armour under ballistic impact. *Composites Part B: Engineering*, 42, 4, 771–780.

Fiedler B, Gojny FH, Wichmann MHG, Bauhofer W, and Schulte K (2004). Can carbon nanotubes be used to sense damage in composites?, *Annales de Chimie*, 29, 81–94.

Gonçalves DP, De Melo FCL, Klein AN and Al-Qureshi HA (2004). Analysis and investigation of ballistic impact on ceramic/metal composite armour, *International Journal of Machine Tools Manufacting*, 2: 44(2–3), 307–316.

Guoxing L and Tongxi Y (2003). *Energy Absorption of Structures and Materials*, Woodhead Publishing, Cambridge, UK.

Hsieh CY, Mount A, Jang BZ and Zee RH (1990). Response of polymer composites to high and low velocity impact, *22nd International SAMPE Technical Conference*, Boston, November 6–8, 14–27.

Hu J (2008). *3D Fibrous Assemblies. Properties, Applications and Modelling of Three Dimensional Textile Structures*, Woodhead Publishing, Cambridge, UK, Number 74, ISBN 978-1-84569-377-0, 115.

Huang CT, Shen CH, Tang CF, and Chang SH (2008a). A wearable yarn-based piezo-resistive sensor, *Sensors and Actuators A: Physical*, 141, 396–403.

Huang CT, Tang CF, Lee MC, and Chang SH (2008b). Parametric design of yarn-based piezoresistive sensors for smart textiles, *Sensors and Actuators A: Physical*, 148, 10–15.

Johnson WS. (1985). Delamination and debonding of materials. *Proceedings of A Symposium High Modulies Fibers and Fracture Testing*, Organised by ASTM Committees D-30 and E-24, respectively, Pittsburgh, Pa, November 8–10, ISBN 0-8031-0414-6.

Kang TJ and Kim C (2000). Energy-absorption mechanisms in Kevlar multiaxial warp-knit fabric composites under impact loading, *Composites Science and Technology*, 4: 60(5), 773–784.

Katragadda RB and Xu Y (2008). A novel intelligent textile technology based on silicon flexible skins, *Sensors and Actuators A: Physical*, 143, 169–174.

Khalid AA (2006). The effect of testing temperature and volume fraction on impact energy of composites, *Material Design*, 27, 499–506.

Ko FK (1989). Three-dimensional fabrics for composites: In Chou TW and Ko FK (eds), *Textile Structural Composites*, Elsevier, New York, 129–171.

Lee JB and Subramanian V (2005). Weave patterned organic transistors on fiber for E-textiles, *IEEE Transactions on Electron Devices*, 62, 269.

Lorussi F, Rocchia W, Scilingo EP, Tognetti A and De Rossi D (2004). *Wearable, Redundant, Fabric-based Sensor Arrays for Reconstruction of body Segment Posture*, IEEE Sensors Journal, 4(6), 807–818.

Lorussi F, Scilingo EP, Tesconi M, Tognetti A, and De Rossi D (2005). Strain sensing fabric for hand posture and gesture monitoring, *IEEE Transactions on Information Technology in Biomedicine*, 9, 372–381.

Medvedovski E (2010). Ballistic performance of armour ceramics: influence of design and structure. Part 2. *Ceramics International* 9: 36(7), 2117–2127.

Miravete A (1999). *3D Textile Reinforcements in Composite Materials*, Cambridge (UK), Woodhead Publishing Limited.

Morye SS, Hine PJ, Duckett RA, Carr DJ and Ward IM (2000). Modelling of the energy absorption by polymer composites upon ballistic impact. *Composites Science and Technology*, 11: 60(14), 2631–2642.

Mouritz AP, Baini C and Herszberg I (1999). Mode I interlaminar fracture toughness properties of advanced textile fibreglass composites, *Composites Part A: Applied Science and Manufacturing*, 30(7), 859–870.

Naik NK and Sekher YC (2000). Damage in woven-fabric composites subjected to low-velocity impact, *Composite Science and Technology*, 60, 731–744.

NF EN ISO 527–4 (1997). *Plastiques–Détermination des Propriétés en Traction, in Partie 4*: Conditions d'Essai pour les Composites Plastiques Renforcés de Fibres Isotropes et Orthotropes: CEN.

Peng S, O'Keeffe J, Wei C, Cho K, Kong J, Chen R, Franklin N, and Dai H (2001). Carbon nanotube chemical and mechanical sensors, in *3rd International Workshop on Structural Health Monitoring*, September 12–14, Stanford, CA.

Ross CA and Sierakowski RL (1973). *Studies on the Impact Resistance of Composite Plates*, ASTM, p. 157–161.

Savage GM (1989). *Fabric and Fibre Reinforced Laminate Armours*, Institute of Metal and Materials, 285–290.

Schueler R, Joshi SP, and Schulte K (2001). Damage detection in CFRP by electrical conductivity mapping, *Composites Science and Technology*, 61, 921–930.

Scilingo EP, Lorussi F, Mazzoldi A, and De Rossi D (2003). Strain-sensing fabrics for wearable kinaesthetic-like systems, *IEEE Sensors Journal*, 3, 460–467.

Shokrieh MM and Javadpour GH (2008). Penetration analysis of a projectile in ceramic composite armour, *Composite Structures* 1: 82(2), 269–276.

Shyr T and Pan Y (2003). Impact resistance and damage characteristics of composite laminates. *Composite Structures* 11: 62(2), 193–203.

Sierakowski RL (1976). Dynamic failure modes in impacted composite plates, In: *Failure Modes in Composite III*, TT Chiao (ed.), AIMMPE, New York, 73–88.

Sun B, Gu B and Ding X (2005). Compressive behavior of 3-D angle interlock woven fabric composites at various strain rates, *Polymer Testing*, 24, 447–454.

Sun B, Liu Y and Gu B (2009). A unit cell approach of finite element calculation of ballistic impact damage of 3-D orthogonal woven composite, *Composites Part B: Engineering* 9: 40(6), 552–560.

Tong L, Mouritz AP and Bannister MK (2002). *3D Fibre Reinforced Polymer Composites*, ISBN 0-08-043938-1, Elsevier Science.

Tsai KH, Chiu CH and Wu TH (2000). Fatigue behavior of 3D multi-layer angle interlock woven composite plates, *Composites Science and Technology*, 60, 241–248.

Vasudev A and Mehlman M (1987). A comparative study of the ballistic performance of glass-reinforced plastic materials, *SAMPE Quarterly*, 18, 4, July.

Wang S and Chung DDL (2006). Self-sensing of flexural strain and damage in carbon fiber polymer-matrix composite by electrical resistance measurement, *Carbon*, 44, 2739–2751.

Wang X, Hu B, Feng Y, Liang F, Mo J, Xiong J and Qiu Y (2008). Low velocity impact properties of 3D woven basalt/aramid hybrid composites, *Composites Science and Technology*, 68, 444–450.

Wilson C (2005). *Improvised Explosive Devices in Iraq: Effects and Countermeasures*, Departments of the Army United States Marine Corps, Field Manual interim, FMI-3–34.119/MCIP 3–17.01, Available from: http://www.fas.org/irp/doddir/army/fmi3-34-119-excerpt.pdf

Zhang W, Suhr J, and Koratkar N (2006). Carbon nanotube/polycarbonate composites as multifunctional strain sensors, *Nanotechnology*, 6, 960–964.

12
Protective clothing for firefighters and rescue workers

C. HERTLEER, S. ODHIAMBO and
L. VAN LANGENHOVE, Ghent University Belgium

Abstract: With the emergence of smart textiles, research into developing more sophisticated equipment and garments for firefighters and rescue workers has evolved. The European Commission has invested in establishing a platform of new technologies to actively monitor operators during their work. This has resulted in several research projects of which the PROeTEX project was the first and this is extensively described in this chapter. Other textile-related research projects to enhance the safety of firefighters are included in this chapter. The result of all this research will be integrated into the protective clothing market in the coming years.

Keywords: smart textiles, wearable sensors, protective clothing for firefighters, PROeTEX.

12.1 Introduction

The main purpose of clothing is to protect the human body against environmental conditions such as rain and cold or sun. So all clothing has a protective function to some extent. For professional workers, however clothing contributes to their personal health and safety as it protects them from the hazardous environment in which they operate. According to the European Standard, EN 340, protective clothing is 'clothing including protectors which cover or replace personal clothing, and which is designed to provide protection against one or more hazards', a hazard being 'a situation which can be the cause of harm or damage to the health of the human body'.

There are many occupations that require specific activities and thus various types and levels of protection. Occupational exposure of the skin to toxic chemicals, for example, will be prevented by wearing appropriate chemical protective clothing; micro-organisms are stopped by protective clothing against biohazards; and firefighters are protected from heat by wearing thermal protective clothing.

Continuous, intensive research and development in the area of personal protective equipment (PPE) has led to considerable improvements over the last few decades. Scientific developments, such as the introduction of

high-performance fibres in the 1960s, have thoroughly changed and improved the level of protection. The biggest revolution for firefighter protection was the use of flame-retardant polymer fibres such as the aromatic polyamides (aramids) and polybenzimidazole (PBI). Meta-aramids (e.g. Nomex by DuPont) and para-aramids (e.g. Kevlar by DuPont, and Technora and Twaron by Teijin) are nowadays widely used fibres. Meta-aramids are known for their good thermal tolerance and long-time stability at high temperatures, and are therefore broadly applied in thermal protective clothing. Para-aramids, on the other hand, are valued for their high tenacity, high modulus and also have good thermal stability at high temperatures, making them suitable for ballistic applications. The introduction of these lightweight fibres has not only increased the level of protection but also the level of (thermal) comfort.

Next to introducing new high-performance fibres, the level of protection can be increased by changing clothing structure, e.g. by using multi-layered fabrics. Firefighter outer garments and trousers consist of an assembly of three layers: flame retardant fabrics are used as an *outer shell* material for the outer garment and the trousers; underneath there is a *vapour barrier* and an *inner thermal barrier*. Firefighter clothes are designed to protect the wearer against heat and flames in the first place, but also against moisture and to some degree against mechanical hazards such as cuts and abrasion.

All these functionalities can be considered as passive methods of protection. But the emergence of new materials and technologies, such as smart textiles and wearable electronics, opens possibilities to further increase the level of protection, this time in an active way. They can be enabled by integrating sensors into the garment for monitoring the firefighter and his close environment, and by setting up a real-time communication with a command post to monitor possible health or other threats.

This chapter mainly describes the work that has been done to merge textiles and electronics into a garment for firefighters and rescue workers within the framework of the European project PROeTEX. Other European projects deal with enhancing the safety of firefighters and their goals are briefly described in what follows. Finally, two commercially available sensorised firefighter garments are described. Also a simulation of the firefighter market for sensorised garments is given.

12.2 The Protection e-Textiles (PROeTEX) project

The perception of a new generation of PPE for firefighters and for rescue workers was framed in the European Integrated Project PROeTEX (Protection e-Textiles): Micro/nano-structured fibre systems for emergency disaster wear. Research into smart textiles and wearable electronics will

play a key role in these developments. So far, the main focus of smart textiles had been in the medical field, for monitoring physiological parameters such as heart and respiration rate in a continuous way and on a daily basis. However, the potential of smart textiles has been further exploited in the field of protective clothing, and PROeTEX was one of the first projects of its kind. The project started in February 2006 and lasted 4 and a half years, until July 2010. The expertise of 23 partners from eight different countries was brought together to achieve the objectives of the project (see Table 12.1). Partners were universities, research institutes, industry and organisations operating in the field of emergency management.

An incremental set of prototype garments was built and tested during the 4 and a half years. A first set of prototypes was ready in July 2007, a second set in December 2008, and a third set in April 2010. Each of the three sets was tested either on a laboratory scale or in field tests.

Apart from developing a successive set of prototypes, also different types of garments were targeted, not only for the rescue workers involved in an

Table 12.1 The PROeTEX project partners

	Partner	Acronym	Country
1	National Institute of Physics of Matter	INFM	Italy
2	Technical University of Lodz	UniLodz	Poland
3	Ghent University	UGent	Belgium
4	Smartex S.r.l.	Smartex	Italy
5	Milior S.p.a.	Milior	Italy
6	Sofileta	Sofileta	France
7	Thuasne France	Thuasne	France
8	University of Pisa	UniPi	Italy
9	Dublin City University	DCU	Ireland
10	Commissariat a l'Energie Atomique	CEA	France
11	Centre Suisse de Electronique et de Microtechnique SA	CSEM	Switzerland
12	Sensor Technology & Device Ltd	STD	UK
13	Steiger	Steiger	Switzerland
14	Philips Research	Philips	Germany
15	Ciba Specialty Chemicals	CIBA	Switzerland
16	Diadora/Invicta Group	Diadora	Italy
17	iXscient Ltd	iXscient	UK
18	Zarlink Semiconductor	Zarlink	UK
19	Brunet-Lion	Brunet	France
20	Brigade de Sapeurs-Pompiers Paris	BSPP	France
21	INSA-Lyon-CNRS	INSA	France
22	EUCENTRE Italian Civil Protection	EUCENTRE	Italy
23	Dept de la Defense et de a Securité Civile	DDSC	France

operation but also for possible victims of an incident. The project involved the development of three types of garments:

- garments for firefighters (urban and forest),
- garments for civil protection rescuers,
- garments for victims (a patch).

The sensorised garments were a combination of available technologies and newly developed textile-based components.

The uniform for the firefighter comprised an outer jacket, an inner jacket and boots. The development was done in close collaboration with the project partner BSPP (Brigade de Sapeurs-Pompiers de Paris, France). EUCentre Italian Civil Protection and DDSC (Dept de la Defense et de la Sécurité Civile, France) were involved in the development of garments for civil protection rescue workers.

12.2.1 The needs of PROeTEX end-users

The PROeTEX project started with interviewing the end-users involved in the project, coordinators from the Italian and French civil protection agencies and managers of the Brigade de Sapeurs-Pompiers de Paris to determine the needs of the firefighters in terms of enhanced safety. Five scenarios in which intervention is critical were hypothesised as follows:

- three for civil protection intervention: violent earthquake and volcano activity in a highly populated area, heavy rain or flooding, and earthquake in a mountain area during winter;
- one for urban firefighter intervention: a large industrial fire;
- one for forest firefighter activity: wild-land fire near populated areas.

The needs could be mainly categorised into two areas, depending on the type of rescue worker:

- monitoring of health status of the wearer and of hazards in the environment;
- localisation of rescue workers when working on an extensive area.

Civil protection workers mainly need to locate all rescue workers when operating in large numbers in a spacious area. The same functionality is important for forest firefighters. In addition, health monitoring is of interest to all firefighters. One of the known types of health failure for firefighters is heat stress. It is caused by the many layers of textiles in their garments. They give the firefighter a very good level of protection; however, they hinder heat dissipation from his body and limit the evaporation of sweat. Actually, the jacket works as a thermal barrier in two ways: from outside to inside but also from inside to outside (Havenith, 1999). When the body

is overheated, a condition of heat stress can occur, which reduces mental performance and slows down the reaction and decision time of the person. The danger can be minimised by measuring some body- and environment-related parameters:

- heart rate, respiration rate, body temperature, etc. from the wearer;
- toxic gases such as CO and CO_2, outside temperature, heat flux through the garment, etc. from the environment.

12.2.2 The PROeTEX integrated system

Nowadays, a typical firefighter uniform comprises a helmet, an outer garment, gloves, trousers and boots. PROeTEX focussed on integrating the major part of the system in only one part of the uniform, the most suitable candidate being the outer jacket. Most of the components of the integrated system can be located there. However, to measure the presence of some toxic gases such as CO_2, the sensor needs to be near to the ground; therefore, some components were integrated into the boots. On the other hand, to measure some physiological data such as heart rate, respiration rate and body temperature, it is obvious that a close contact with the skin is required. For this reason, it was soon clear that the PROeTEX uniform should include an inner garment, next to an outer garment and a pair of boots.

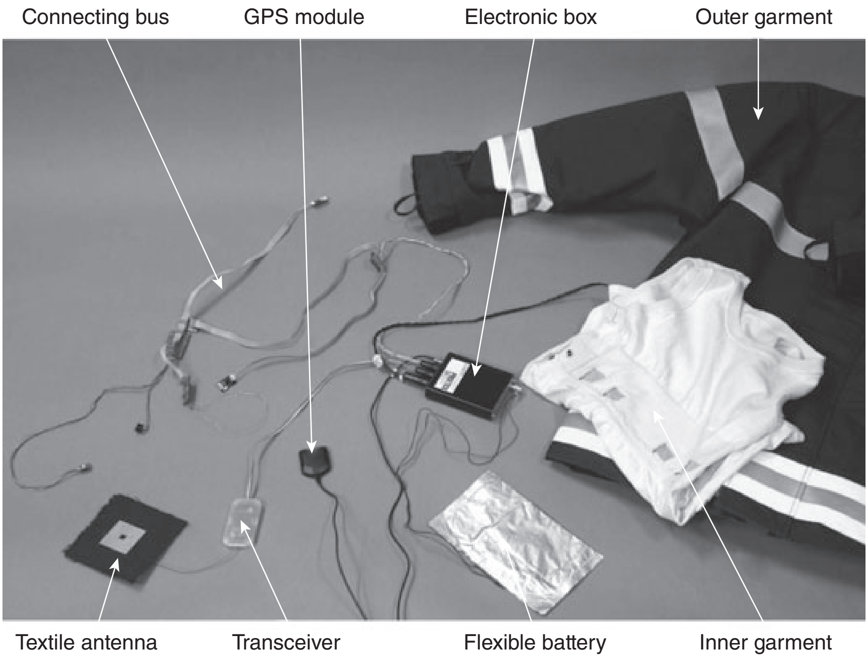
In most cases, a T-shirt or some kind of inner garment is not part of the uniform of a firefighter. However, BSPP; being part of the French military makes an exception: their uniform includes a cotton T-shirt. This means that for these firefighters, the inner garment of the PROeTEX uniform was not an unusual extra piece of uniform.

The outer garment of a firefighter is typically made out of several layers of textiles with distinct functionalities:

- the outer shell is the first level of protection for the firefighter and needs to give flame, thermal and even mechanical resistance;
- a moisture barrier is meant to keep the firefighter dry, or at least to protect him from water or from other liquids approaching him from the outside;
- the thermal liner prevents the transfer of heat from the environment to the body.

In order not to perforate the different layers, all components of the PROeTEX system were integrated between the second and the third layer of this assembly. In this way, the electronics are also protected by the moisture barrier from water coming from the environment.

The first set of prototype uniforms (Fig. 12.1) were delivered 18 months after the start of the project. They were based mainly on commercially



12.1 The first PROeTEXfirefighter prototype with all its sensors and components.

available components, completed with technologies already developed by the project partners in former projects and some new components that had been developed during the first project period.

During the following months, the uniforms were comprehensively tested both in laboratory and in field conditions organised in the specific training centres such as the Firefighter training centre of Paris in St Denis, France, for the urban fire scenario and in the Research Centre of the French Civil Protection (CEREN) in Gardanne, France for the forest fire scenario. The latter was done by the end-users themselves, the Italian and French civil protection and the firefighter department of Paris BSPP. The tests are fully described in Curone *et al*. (2008). The outcomes of the tests were used to improve the second set of uniforms that were delivered at the end of 2008. Again, the system was validated from a technological point of view and from a usability point of view by the researchers and by the end users (Curone *et al*., 2010). Improvements and adaptations were done and led to a third and final set of prototype uniforms, which were delivered in April 2010.The last months of the projects were dedicated to their testing, both in laboratories and in simulated firefighter scenarios (Magenes *et al*., 2010). (Fig. 12.2)

12.2 During field testing of the PROeTEXfirefighter prototypes.

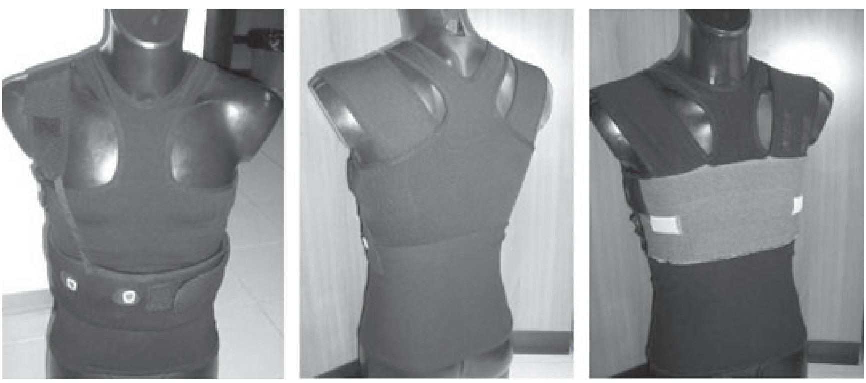
A more detailed description of the PROeTEX garments and their integrated components is given in the following section.

The inner garment

The inner garment (IG) (Fig. 12.3) incorporates the physiological sensors that are needed to monitor the health status of the wearer. To do so, a close contact with the skin is essential. In order to achieve this, the region around the torso is manufactured in a highly elastic material. The close contact with the skin also means that attention needs to be given to the sensation of comfort because this will be a key factor in the acceptance of wearing the system. The first T-shirt was based on cotton; however, to increase the protection level, a blended yarn of aramid and cotton was the basis for the following prototypes (Fig. 12.4). The first shirt comprised sensors for heart rate, respiration rate and body temperature but, during the project, additional sensors were developed and integrated into the garment. They are listed in Table 12.2.

The *heart rate (HR) electrodes* are textile electrodes based on electroconductive stainless steel yarn that is knitted into the inner garment by using

12.3 The first PROeTEX inner garment with: I1 – textile electrode for measuring heart rate; I2 – piezoresistive sensor for measuring breathing rate; I3 – thermocouple for measuring body temperature.



(a) (b) (c)

12.4 Examples of prototypes of the inner garments for Italian and French civil protection employees.

Table 12.2 Components in the inner garment for the three successive prototypes

First	Second	Third
Cotton-based T-shirt	Aramid-based T-shirt	Aramid-based T-shirt
Heart rate electrode	Heart rate electrode	Heart rate electrode
Breathing rate sensor (piezoresistive)	Breathing rate sensor (piezoresistive and piezoelectric)	Breathing rate sensor (piezoresistive and piezoelectric)
Body temperature sensor	Body temperature sensor	Body temperature sensor
	SpO_2 sensor	SpO_2 sensor
		Dehydration detector
	Vital signs board (VSB)	VSB
	Wired (bus) connection between VSB and Personal Electronic Box (PEB)	Wireless connection between VSB and PEB

a tubular intarsia technique. The electrodes are knitted double face and the outer part of the electrode does not contain electroconductive yarn so that it is insulated from the environment. These two knitted layers do not touch, so they create a kind of pocket. The insulating side of the electrode is made out of a blended yarn: 50% meta-aramid Nomex® from DuPont and 50% flame-retardant viscose. To maximise the contact between the electrode and the skin, a hydrogel membrane was used in the first prototype (Loriga *et al*., 2005). For the next prototypes, the electrode fabrication method was improved and a Neoprene filler was inserted into the aforementioned pocket to guarantee a good contact with the skin without using the hydrogel.

The *breathing rate (BR) sensor* is based on two different technologies. The first one is a *piezoresistive* textile sensor, positioned around the chest and integrated into the inner garment. Slight variations in length and shape because of thoracic and abdominal circumference changes during breathing alter the resistance of the sensor (Pacelli *et al*., 2006). The second approach assures a more reliable breathing signal because it is based on *a piezoelectric transducer* in wire form. In the third set of prototypes, this piezoelectric polyvinylidene fluoride (PVDF) sensor was integrated, together with the electronics, as *the Vital Signs Board (VSB)* in a detachable belt (Fig. 12.5) that is carried around the chest. It easily opens and closes with a Velcro strip and it has an adjustable strip over one shoulder. In this elastic sensing region, *the interconnections* between the sensors and the electronics have been achieved with two specially designed elastic conductive yarns, integrated during the knitting process. The elasticity is obtained through an elastic core material (Lycra®) and the conductivity comes from a stainless

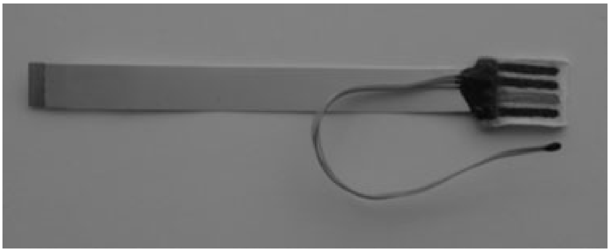
12.5 Belt with piezoelectric sensor and vital signs board (VSB), wirelessly connected to the Personal Electronic Box (PEB).

steel monofilament that is twisted around the core. Electrical insulation is obtained by covering the yarns with polyester.

The *skin temperature* is measured with a commercially available thermocouple (LM92, by National Semiconductor) placed at the armpit. Different packaging has been tried to minimise the interference with the environmental temperature. Good skin contact is ensured by the elastic belt.

The *dehydration sensor* measures the sodium concentration in sweat. During an intervention, the emergency personnel can be exposed to extreme physical action, with dehydration as an important consequence. An abnormal loss of sodium in the sweat can lead to a hypo- or hyper-natremia. To be wearable and integratable into the inner garment, a textile-based electrochemical sensor (Fig. 12.6) was developed. A metallic coating was chemically deposited on a 95/5% cotton/elastane fabric. The electrochemical cell is made of four electrodes of which three are working electrodes and one is a reference electrode. The cell is coupled to a temperature sensor to enhance the reliability because electrochemical measurements are temperature dependent.

The working electrodes carry a host molecule which is able to selectively trap Na^+ ions. This functionalised electrode is an Ionic Selective Electrode.



12.6 Electrochemical cell made of three working electrodes and one reference electrode. The temperature probe is attached to it.

The electrochemical cell is connected to a portable electronic board which drives the sensing part and achieves the signal processing to convert the electrical information into sodium ion concentration (Marchand *et al.*, 2009).

The SpO_2 sensor measures the amount of oxygen carried by blood cells in the arterial blood. To do this, a non-invasive technique involving pulse oximetry (i.e. SpO_2) is used. Commonly, this technique requires the use of an optical sensor placed around the fingertip of the patient. CSEM have developed a reflectance pulse oximeter that can be placed at body locations such as the breastbone. This allows integration of the sensor into the inner garment. The sensor is an optical transducer based on controlled-source electromagnetics technology. A unit with several pairs of optical emitters and receivers is integrated at the breastbone level of the inner garment. There, a processor selects the best signals and stores the values in a memory.

During the project, the architecture of the inner garment evolved, in terms of materials and in terms of design. Finally, two different inner garments were developed,

The outer garment

The outer garment (OG) comprises a different set of sensors and other electronic components (Table 12.3).

The system is entirely integrated under the moisture barrier of the garment. As such, all components are also protected against liquids from the environment. Because the different components are interconnected with electroconductive wires, all components are fixed between the same fabric layers so that the fabrics do not need to be perforated.

A modified platinum sensor array is integrated into the outer garment to simultaneously monitor the *environmental temperature* and the *heat flux* through the jacket. The sensors used are Pt1000 platinum resistors (temperature sensors to the Pt 1000 Ω standard from Atexis), which have a

Table 12.3 Components in the outer garment for the three successive prototypes

First	Second	Third
External temperature sensor	External temperature sensor	External temperature sensor
	CO sensor	CO sensor
	Heat flux sensor	Heat flux sensor
GPS module	GPS module	GPS module
	Visual alarm	Visual alarm
	Acoustic alarm	Acoustic alarm
Accelerometers (in collar and wrist)	Accelerometers (in collar and wrist)	Accelerometers (in collar and wrist)
	Motion sensor (textile)	Motion sensor (textile)
	ZigBee module	ZigBee module
Personal Electronic Box (PEB)	PEB	PEB
Textile antenna, one	Textile antenna, one	Textile antenna, two

positive temperature coefficient, i.e. the resistance value increases when the temperature rises (Oliveira *et al*., 2010).

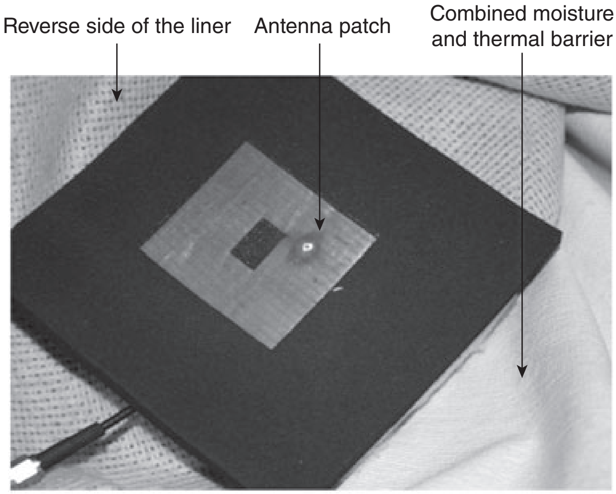
A heat flux sensor gives information about how heat propagates from the environment through the garment. When heat escapes from the body, a positive heat flux is measured. This is the normal situation. The human body removes over-production of metabolic heat to avoid an increase of the internal temperature. Consequently, a negative heat flux means that heat is entering the body from the environment. This results in an increase of the core temperature. An increase of 1.5 °C in relation to the core temperature of the firefighter at the beginning of the intervention, triggers an order to leave the fire (Oliveira *et al*., 2009).

The *user's activity* is measured by means of two tri-axial accelerometers, one of which is placed in the collar of the jacket and the other in the left sleeve. Different activities, such as standing, walking or running, can be distinguished. An alarm is generated when the firefighter is 'down'.

The *GPS module* is meant to be able to locate the rescue worker in an outdoor environment such as a forest. It does not function when the rescuers approach high buildings or other kinds of dense obstacles such as thick vegetation in a forest.

The electronic heart of the system is *the professional electronic box (PEB)*, which collects the data from all the sensors both in the IG and in the OG.

A *planar textile-based antenna* (Fig. 12.7) is connected to a Bluetooth module and transmits the data collected by the PEB to a remote monitoring station. The first prototype incorporated only one antenna, which was in the front of the garment; however, to ensure optimal data communication, a



12.7 Textile antenna integrated between the moisture barrier and the liner.

second antenna was later added in the back of the garment. The antenna operates in the 2.45 GHz ISM band and is a microstrip patch antenna (Hertleer *et al*., 2009). The size of the antenna patch is about 5 cm by 5 cm and it is made of an electroconductive material, which can be a textile or a printed surface (screen printed with silver-based electroconductive ink). Several substrate materials were explored during the project, but flexible foam seemed to be most suited. Bending the antenna, and the presence of the human body or of moisture had no adverse effects on the antenna characteristics (Hertleer *et al*., 2010).

The prototypes were equipped with a lithium ion-polymer *battery* which was effective for up to 7 hours to power the garment's electronics. Within the project, CEA developed and delivered flexible textile compatible batteries that were able to power all electronic devices embedded in the firefighter outer garment during a period of two hours, with a maximum useful capacity of about 900 mAh for 360 cm^2 surface.

The *visual and acoustic alarms* integrated into the garment are to warn the wearer if something goes wrong.

The boots

The boots have been manufactured by one of the project partners. In the final arrangement they comprise two types of sensors (Table 12.4): to measure the presence of toxic gases, such as CO_2, that are heavier than air

Table 12.4 Components in the boots for the three successive prototypes

First	Second	Third
CO_2 sensor	CO_2 sensor ZigBee module housing	CO_2 sensor ZigBee module housing

and are found near the ground, and to measure the activity of the wearer. The module is based on a CO_2-D_1 Alphasense sensor, together with a processor for data acquisition and processing, and a ZigBee module to communicate wirelessly with the PEB in the outer garment.

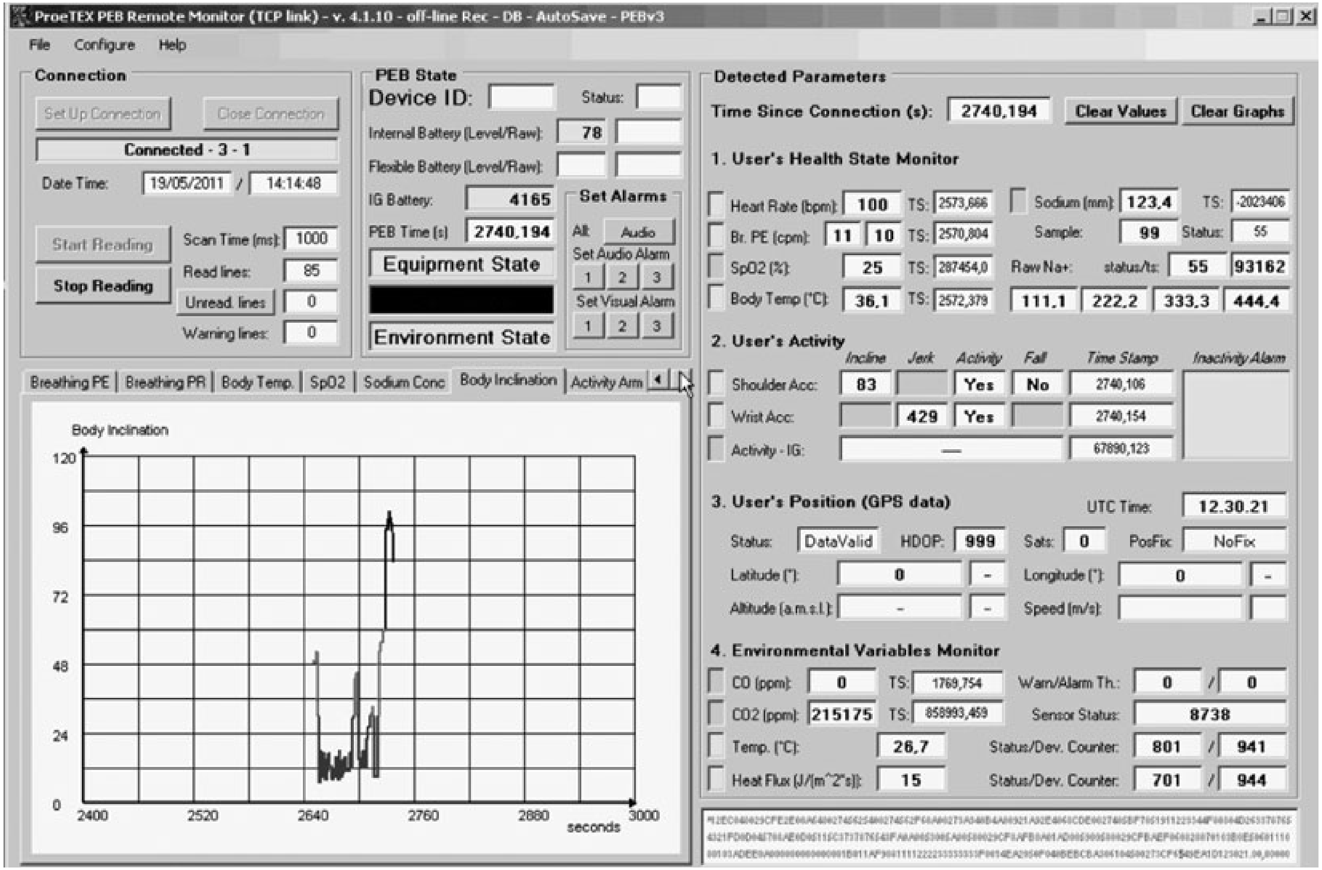
The PROeTEX monitoring software

The data recorded by the sensors in the wearable system are transmitted through a long-range communication system (Magenes *et al*., 2009) to a computer in the command post. The monitoring software produces a visual representation of the data measured by the PEB, as shown in Fig. 12.8. A colour code red draws attention to things that are going wrong. Detailed information is given in four groups: about the user's health status, about the user's activity, about the user's position and about the environment. For each of the group of sensor data, a graph shows how the values change over time. In Fig. 12.8, the body inclination is in a dangerous zone, meaning that the firefighter might be lying down. The 'User State' flashes red to get the attention of the commander.

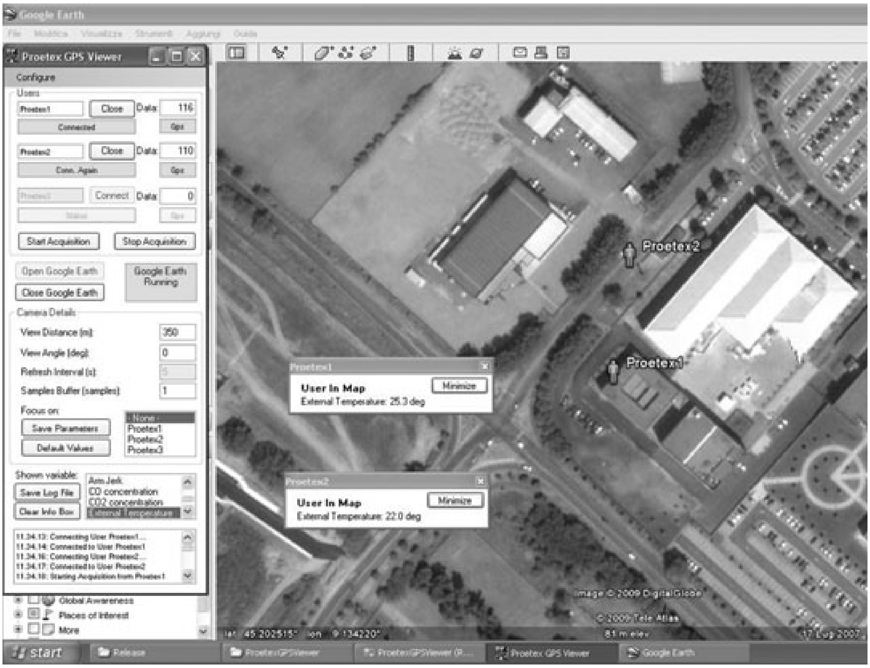
The position of the PROeTEX firefighter is visualised on a graphic interface based on Google Earth software and is shown in Fig. 12.9. A small icon follows the track of the wearer as he moves around the disaster area.

The victim patch

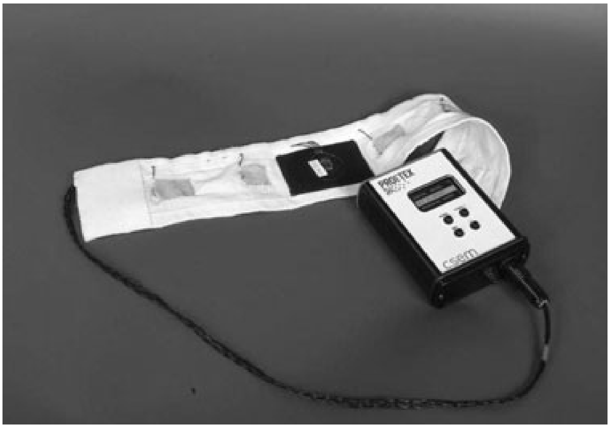
In addition to monitoring the health status of rescue personnel, victims should be monitored. Therefore, a victim patch (Fig. 12.10) has been developed within the PROeTEX project, using the same technologies but integrated in a different way. The victim patch is a textile belt that can easily be put around the chest of a victim to monitor vital signs. Therefore, it contains sensors to measure heart rate, breathing rate and body temperature. The sensors that are used here are the same as those of the firefighter inner garment. A dedicated *victim electronic box (VEB)* processes the sensor's data and transmits them to the monitoring station by means of an integrated Bluetooth module.



12.8 Window of monitoring software providing information on the status of the wearer and his environment; data provided by the sensors.



12.9 Window of monitoring software showing the position of the wearer.



12.10 Textile victim patch with VEB.

12.3 Other firefighter-related European projects

12.3.1 I-Protect

The I-Protect project (EU FP7-NMP Project I-Protect, 2009–2013) for PPE was launched on 1st October 2009. It ends in November 2013. The PPE will ensure active protection and provision of useful information. It is most applicable to high-risk and complex environments such as firefighting, mining and chemical operations. The main risks include explosions, high temperatures, dangerous chemicals released, smoke, dust, high humidity and limitation of breathable fresh air. The project aims at integrating advanced materials with sensors for real-time monitoring of exposure to risk in the surroundings e.g. temperatures, gas and oxygen levels. The sensors will also measure changes in protection aspects, such as air pressure in compressed units. Materials used for the sensors will be optical fibres and micro-sensors, integrated with textiles. Carbon nanotubes will be incorporated into materials for functionalisation and achieving aspects such as conductivity of the material.

Partners

There are a total of 16 partners involved in this project (Table 12.5), with about seven institutions, the rest being either industries or a network of industries having a common interest.

Table 12.5 I-Protect partners

	Partner	Country
1	Institute of Biomechanica Valencia	Spain
2	Central Institute for Labour Protection	Poland
3	Finnish Institute of Occupational Health	Finland
4	Institute of Mining Technology	Poland
5	Federal Institute for Materials Research and Testing	Germany
6	Centralna Stacja Ratownictwa Górniczego S.A	Poland
7	NeoVision Sławomir Zwolenik	Poland
8	Fundacion LEILA	Spain
9	Gruppo Colorobbia	Italy
10	Sperian Respiratory Protection	France
11	German Fire Protection Association	Germany
12	Safibra	Czech Republic
13	Orneule Company	Finland
14	Aero Sekur	UK, Italy
15	Coalesenses Gmbh	Germany
16	Orlene Company	Poland

Project expected results

The results of the project are to address the safety of firefighters, miners and rescue squads. Special sensors will be developed and combined with a wireless system for detection and communicating on hazardous gases and temperature changes during rescue operations. Both physiological and working environment parameters will be transmitted via a dedicated wireless system to the rescue coordination centre in order to allow the supervision of the rescue activities and health of different members of the rescue team. Utilising nanomaterials will allow the development of sensors that will measure the amount of toxic gas in the environment.

12.3.2 ProFiTex

The project ProFiTex started on 1st October 2009 and has a duration of 36 months (EU FP7-NMP Project ProFiTex 2009–2012).This project also deals with improving the safety of the firefighters. The approach of the project is based on professional user (firefighter) involvement in designing and evaluating the safety of their equipment. The design will be adopted from the European wearIT@work project (EU FP6-IST Project wearIT@work, 2004–2008) and improved further by creating innovative systems for data transmission and tactical navigation. This will enhance the communication between the firefighters' front line, their group leaders and the commander hierarchy.

Prototype

The ProFiTex system to be developed comprises two main components: a fire fighting jacket with integrated sensors, electronics, and a *'Smart LifeLine'*, which is a braided rope with a double function: as a security rope and as a medium to transmit data and energy. Inside the *Smart LifeLine,* several beacons will be embedded. These beacons enable the navigation of the firefighters in smoky environments and the exchange of information with the group commander. One firefighter is physically connected to the rope; he also wears an infrared camera on his helmet. The other firefighters wear electronics that can pick up the signals emitted by the beacons. A helmet-mounted display shows the firefighter where the beacons are and thus the way back, out of the fire. The navigation system has been tested successfully at a workshop in December 2010, where professional firefighters were deployed.

The ProFiTex system comprises electronic devices such as localisation sensors, communication devices and a human–computer interface device integrated into the firefighters' jackets. Since wireless communication is

Table 12.6 Project ProFiTex partners

	Partners	Country
1	Active Photonics AG, visualisierungs-kommunikationssysteme	Austria
2	D'Appolonia S.p.A.	Italy
3	Texport Funktionsbekleidung GmbH	Austria
4	Centro Tecnológico Leitat (Lei), Leitat	Spain
5	The Fraunhofer Institute for Applied Information Technology	Germany
6	Sabine Gross (Heat)	Germany
7	LABOR S.r.l. (Lab)	Italy
8	RWTH Aachen University	Germany
9	The Swiss Federal Institute of Technology, Zurich	Switzerland
10	TexClubTec	Italy
11	Vienna University of Technology	Austria

difficult over long distances and through several walls of a building, an innovative method to transmit information will be applied.

Partners

There are a total of 11 partners, comprising 3 industries and 8 institutions, (Table 12.6).

12.3.3 Safeprotex

The project started on 1st April 2010 and it is to run for 42 months, up to October 2013 (EU FP7 NMP Project Safeprotex, 2010–2013). The Safeprotex project is concerned with research on highly protective clothing worn during complex operations. The main idea of the project is to address the problems that current protective garments are facing – such as new risks, due to advances in technology and climate change – by innovative solutions. The Safeprotex clothing is designed for rescue teams and emergency operators.

The scope of the research is limited to three areas:

- emergency operations under extreme weather conditions (e.g. floods, hail),
- operations under the risk of wild land fires,
- first aid medical personnel potentially exposed to any type of risk.

Partners

There are 18 participants (Table 12.7) in this project.

Table 12.7 Project Safeprotex partners

	Partners	Country
1	Clothing Textile and Fibres Technological Development SA	Greece
2	Inotex S.R.O., DVUR Kralove Nad Labem	Czech Republic
3	SARL SCIC Rescoll	France
4	TDV Industries	France
5	De Montfort University Textile Engineering and Materials (Team) Research Group	United Kingdom
6	TUT – Tampere University of Technology	Finland
7	Fundacion Gaiker	Spain
8	Swerea Ivf Ab	Sweden
9	Next Technology Tecnotessile Societa Nazionale Di Ricerca R.L.	Italy
10	Acondicionamiento Tarrasense Leitat	Spain
11	Lenzi Egisto S.P.A.	Italy
12	VUCHV – Vyskumny Ustav Chemickych Vlakien, A.S.	Slovak Republic
13	Calsta Workwear SA	Greece
14	Nanothinx SA – Research and Development of Carbon Nanotubes S.A.	Greece
15	Suministros Irunako, S.C.	Spain
16	Fundacio Privada Cetemmsa	Spain
17	ONGD SAR Espana	Spain

Expected project outputs

The goal of Safeprotex is to develop highly effective PPE for people who operate under complex emergency situations. The garments aim to provide protection against multiple hazards, present extended useful lifetime and ensure physiological comfort of the wearer. The research will take a bottom up approach, where possibilities of developing new fibres with different functionalities are investigated. Among these are bicomponent fibres, chitosan fibres, and fibres that incorporate multiwall carbon nanotubes (MWCNTs). The project will look into the entire value chain (spinning, weaving, surface treatment technologies and design), up to the prototyping of the actual protective uniforms. The approach will be based on user requirements. Other established safety level requirements are against foul weather conditions, microbial contamination, and protection against low temperatures, poor visibility, mechanical instability and chemical attack.

12.3.4 Prospie

This project was launched in September 2009 and it is to run for three years. The Prospie project aims at improving the comfort of firefighters by

Table 12.8 Project Prospie partners

	Partner	Country
1	Bel-confect	Belgium
2	Capzo	Netherlands
3	D'Appolonia	Italy
4	Empa – Eidgenössische Materialprüfungs- und Forschungsanstalt	Switzerland
5	ErgonSim	Germany
6	Foritas	Lithuania
7	Humanikin	Switzerland
8	HVC – Henk Vanhoutte Consulting	Belgium
9	ICOP	Italy
10	ifak system	Germany
11	LU – Loughborough University	UK
12	LTI – Lithuanian Textile Institute	Lithuania
13	Merford Cabins	Netherlands
14	Pakaita JSC	Lithuania
15	Palemonokeramika	Lithuania
16	TNO	Netherlands

absorbing or removing the excess heat that the firefighter is exposed to. This will enable him or her to work longer wearing protective clothing, feeling less discomfort. In addition to sensors in the PPE that will alert the worker, innovative cooling methods will be investigated (cooling salts, phase-change materials and ventilation cooling). These will be incorporated into the PPE.

Prospie aims at developing an improved PPE, disseminating the results to standardisation organisations, industry and public procurement organisations. It also aims at developing a training programme for SMEs and end-users for acceptability of the system.

Partners

This project involves 16 partners (Table 12.8) located within European countries.

Prototype

The Prospie system demonstrator, Protective Responsive Outer Shell for People in Industrial Environments and Multi-Layer Sensor Array, is provided by ifak system GmbH (http://www.youtube.com/watch?v=syBXs51aEic).

12.4 Simulation of the firefighter market

Within the European Coordination Action project Systex (EU FP7 ICT Project Systex 2008–2011), a simulation tool was developed to estimate the

value of market growth. The firefighter market was selected to work with because it is a mature market. The total market value is determined by:

- the number of potential users,
- the fraction of those users actually buying the product,
- the price of the product.

The models start from estimates of the above mentioned factors, as well as their expected evolution in time.

For the firefighter market, a distinction has to be made between large fire brigades operating in cities (mainly professionals) and small brigades operating in rural areas (usually volunteers). The bigger brigades replace their equipment more often (every five years) and are able to afford more high-tech suits. This is in contrast to the equipment of volunteers, which serves considerably longer; up to 10 years or even more.

In Europe there are:

- 385 000 professional firefighters,
- 2 200 000 volunteers.

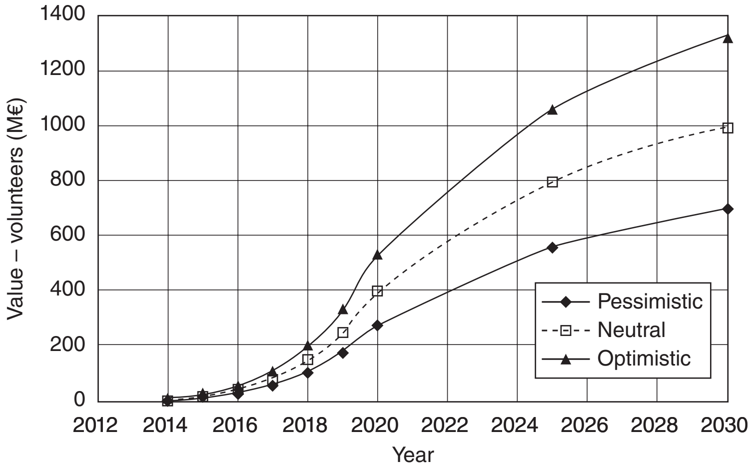
These numbers are not expected to change significantly over the next few years. So the market is mature. The price of a high-tech suit is thought to be €1000. A 'lighter' version with some basic functions, such as heart and respiration rate sensors and a basic alarm function, could have a lower price of *ca*. €600. The price will slowly decrease because of the scale factor. On the other hand the decrease will be limited because the level of complexity and intelligence will increase.

Simulations have been made for forecasting the market value for smart firefighter suits. They take into account the number of firefighters and the fraction wearing the smart suit as well as price evolution. The simulation for the market evolution in Europe for PPE for volunteer firefighters is shown in Fig.12.11 and that for professionals in Fig. 12.12. The graphs show three lines: one considering a pessimistic, one a neutral and one an optimistic scenario.

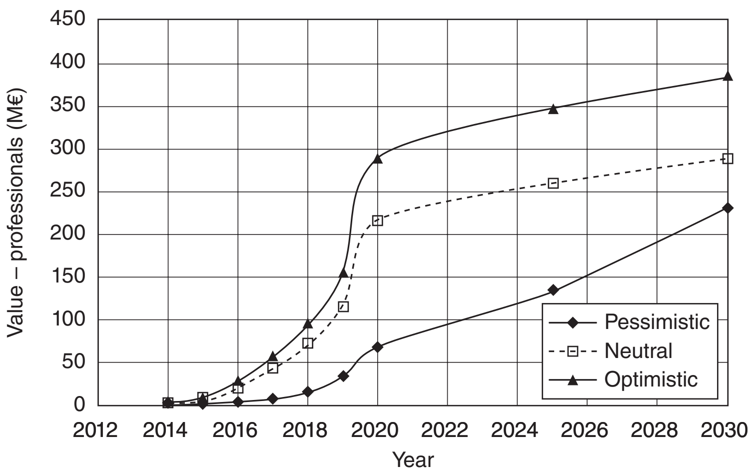
The conclusion of these simplified simulations is that, in spite of the lower price of the product and the lower replace rate, the total market value is considerably higher for volunteers.

12.5 The Viking fire protection suit with built-in thermal sensor technology

The Danish company Viking has introduced a suit with in-built thermal sensor technology (TST) (Fig. 12.13). 'Integrated thermal sensors in the inner and outer layers of the coat monitor heat near the fire-fighter, as well as inside the coat close to the body. Sensors are attached via a conductive ribbon to LED displays on the sleeve and back of the left shoulder. The



12.11 Market evolution in Europe for PPE for volunteer firefighters.



12.12 Market evolution in Europe for PPE for professional firefighters.

shoulder LED display is visible to other fire-fighters, indicating to them potentially dangerous situations. The LED on the lower sleeve indicates elevated heat levels both inside and outside their fire suit. As an indication, the display's outer circle flashes slowly when external temperatures reach about 250 °C. Indicating the precious seconds between safety and injury, at 350 °C, it flashes rapidly. When the temperature inside the garment reaches about 50 °C, the long line on the display flashes slowly. At 68 °C it flashes rapidly. A small box in the inner liner of the coat contains a battery and an innovative control chip that calculates temperature and activates the LED

12.13 Viking firefighter suit with built-in thermal sensor technology.

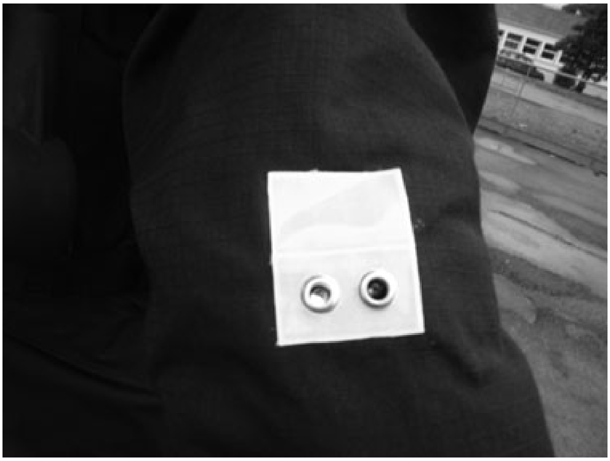
displays. Sensors are protected by a flexible waterproof and heat resistant thermo plastic material. No maintenance is required, only the battery needs to be changed. The durable fire suit with built-in TST microelectronics can withstand at least 25 wash cycles.' (Viking, 2007).

12.6 The Tecknisolar firefighter garment

The French company Tecknisolar Seni (Tecknisolar, 2011) located in Saint-Malo, France, has introduced a sensorised firefighter garment (Fig. 12.14). On the outside of the jacket, a temperature sensor measures the environmental temperature; inside the jacket, the internal temperature is measured. A 'man down' detector is integrated, together with a gas sensor (Fig. 12.15). A thermographic camera indicates the environmental temperature in real time and is built into the helmet.

The purpose of the system is to avoid heat stress for the firefighter. The system warns him in extreme situations to withdraw from the fire. The

12.14 Integrated gas sensor.



12.15 Tecknisolar sensorised firefighter suit.

jacket has proven its efficacy in a marine training centre in Brest, France and is being further tested.

12.7 Conclusion

This chapter has made clear that in Europe a lot of research effort is put into elaborating the safety of firefighters and rescue workers. Much of this is done by integrating sensors for monitoring the wearers' health status and their environment into the high-performance garments they are already equipped with. The PROeTEX project was the first in its kind, and many

other projects have followed since then. Some sensorised garments are already available on the market and the market evolution predicts that there will be a strong interest in this kind of smart garment in the future.

12.8 References

Curone, D., Dudnik, G., Loriga, G., Magenes, G., Secco, E. L., Tognetti, A. and Bonfiglio, A. (2008) 'Smart garments for emergency operators: results of laboratory and field tests', *30th Annual International Conference of the IEEE Engineering in Medicine and Biology Society*, *1–8*, 494–497.

Curone, D., Secco, E. L., Tognetti, A., Loriga, G., Dudnik, G., Risatti, M., Whyte, R., Bonfiglio, A. and Magenes, G. (2010) 'Smart garments for emergency operators: the PROeTEX project', *IEEE Transactions on Information Technology in Biomedicine,* 14(3), 694–701.

Havenith, G. (1999) 'Heat balance when wearing protective clothing', *Annals of Occupational Hygiene,* 43(5), 289–296.

Hertleer, C., Rogier, H., Vallozzi, L. and Van Langenhove, L. (2009) 'A textile antenna for off-body communication integrated into protective clothing for firefighters', *IEEE Transactions on Antennas and Propagation,* 57(4), 919–925.

Hertleer, C., Van Laere, A., Rogier, H. and Van Langenhove, L. (2010) 'Influence of relative humidity on textile antenna performance', *Textile Research Journal,* 80(2), 177–183.

Loriga, G., Taccini, N., De Rossi, D. and Paradiso, R. (2005) 'Textile sensing interfaces for cardiopulmonary signs monitoring', *2005 (27th) Annual International Conference of the IEEE Engineering in Medicine and Biology Society,* 1–7, 7349–7352.

Magenes, G., Curone, D., Caldani, L. and Secco, E. L. (2010) 'Fire fighters and rescuers monitoring through wearable sensors: the PROeTEX project', *2010 Annual International Conference of the IEEE Engineering in Medicine and Biology Society (EMBC)*, 3594–3597.

Magenes, G., Curone, D., Lanati, M. and Secco, E. L. (2009) 'Long-distance monitoring of physiological and environmental parameters for emergency operators', *2009 Annual International Conference of the IEEE Engineering in Medicine and Biology Society (EMBC),* 1–20, 5159–5162.

Marchand, G., Bourgerette, A., Antonakios, M., Rat, V., David, N., Vinet, F. and Guillemaud, R. (2009) *Development of a Dehydration Sensor Integrated on Fabric,* translated by Berkeley, CA, United States:IEEE Computer Society, 230–233.

Oliveira, A., Gehin, C., Delhomme, G., Dittmar, A. and McAdams, E. (2009) 'Thermal parameters measurement on fire fighter during intense fire exposition', *2009 Annual International Conference of the IEEE Engineering in Medicine and Biology Society (EMBC),* 1–20, 4128–4131.

Oliveira, A., Gehin, C., Massot, B., Ramon, C., Dittmar, A. and McAdams, E. (2010) 'Thermal parameters measurement on fire fighter: improvement of the monitoring system', *2010 Annual International Conference of the IEEE Engineering in Medicine and Biology Society (EMBC)*, 6453–6456.

Pacelli, M., Caldani, L. and Paradiso, R. (2006) 'Textile piezoresistive sensors for biomechanical variables monitoring', *2006 (28th) Annual International Conference of the IEEE Engineering in Medicine and Biology Society,* 1–15, 3892–3895.

13
Advances in chemical and biological protective clothing

Q. TRUONG and E. WILUSZ, US Army, USA

Abstract: Protection against hazardous chemical and biological (CB) materials is necessary in many aspects of everyday life and can be provided by the proper selection of protective clothing. Variables to be considered include weight, comfort, level of protection, and the duration of protection required. To cover the range of situations that may be encountered, a spectrum of CB protective materials and clothing systems has been developed. This chapter reviews the types of materials and clothing systems currently in use and the science and technology efforts underway to maximize protection and comfort.

Key words: chemical protective clothing, biological protective clothing, chemical protective materials, biological protective materials.

13.1 Introduction

Protection against hazardous chemical and biological (CB) materials is necessary in many aspects of everyday life. Proper protective clothing is needed during household chores and in industrial, agricultural, and medical work, during military operations; and in response to incidents of terrorism. This clothing generally involves a respirator or dust mask, hooded jacket and trousers or one-piece coverall, gloves, and overboots, individually or together in an ensemble. Many different types of materials and garment designs are used in these clothing items, and protection levels vary considerably. Choices must be made as to which items of protective clothing to select for a given situation or environment. Variables to be considered include weight, comfort, level of protection, and the duration of protection required. In addition, the nature of the challenges to be encountered is also of significant consideration. Due to the large number of variables involved, a spectrum of CB protective materials and clothing systems has been developed. Fully encapsulating ensembles made from air impermeable materials with proper closures provide the highest levels of protection. These latter ensembles are recommended for protection in situations where exposure to hazardous chemicals or biological agents would pose an immediate danger to life and health.

Chemical warfare agents (CWAs) such as chlorine, phosgene, and mustard gas (also known as blistering agent), were used in World War I (WWI). As

Published by Woodhead Publishing Limited, 2013

Table 13.1 Formulae of some traditional chemical agents

Chemical agents	Formula
Sulfur mustard	$(ClCH_2CH_2)_2S$
Sarin	$C_4H_{10}FO_2P$
Soman	$C_7H_{16}FO_2P$
VX	$C_{11}H_{26}NO_2PS$

a result there were over a million casualties, with approximately 90 000 deaths.[1] Nerve agents, consisting of organophosphorus compounds, were developed during the 1930s.[2] CWAs were not used during WWII. There are many examples of CWA use from historical records. Italy sprayed mustard gas from aircraft against Ethiopia in 1935. Japan used CWAs when they invaded China in 1936. Egypt used phosgene and mustard gas bombs in the 1960s in the Yemeni Civil War. During the Iran–Iraq war between 1980 and 1988, Iraq used sulfur mustard and probably nerve agents on their own Kurdish civilians in northern Iraq and in the city of Halabja.[3] It was reported that 5000 civilians were killed. The Aum Shinrikyo cult used Sarin nerve agent to terrorize Matsumoto City in 1994 and then attacked the Tokyo subway system in 1995. The Tokyo subway incident exposed some 5–6000 people and killed 12.[4] In 2002, 115 people died as a result of the Russian government's use of the chemical BZ, a 'knockout gas,' to subdue about 50 Chechen armed guerillas holding about 800 Russians hostage in a Moscow theater. The chemical formulae of some traditional agents are provided in Table 13.1.

The use of biological warfare agents (BWAs) has been recorded as early as the 6th century BC when the Assyrians poisoned enemy wells with rye ergot. In 1937, Japan used aerosolized anthrax in experiments on prisoners. There were several cases of suspected 'yellow rain' incidents in Southeast Asia, and the suspected use of trichothecene toxins (T2 mycotoxin) in Laos and Cambodia. In 1978, ricin was used as an assassination weapon in London. In 1979, there was an accidental release of anthrax at Sverdlovsk. In 1991, Iraq admitted its research, development, and BWA weapons production of anthrax, botulinum toxin, Clostridium perfringens, aflatoxins, wheat cover smut, and ricin to the UN. In 1993, a Russian BW program manager, who had defected, revealed that Russia had a robust biological warfare program, including active research into genetic engineering and binary biological weapons.[5]

Recent military concerns have included toxic industrial chemicals (TICs) as emerging threats where TICs include chemicals such as common acids, alkalis, and organic solvents. However, it should be noted that TICs have

long been a concern for military personnel, civilian emergency responders, and industrial chemical handlers. Next generation CB protection is being developed with TIC protection very much in mind.

13.2 Current chemical and biological (CB) protective clothing

There are many different types and designs of CB protective clothing that are available to both the military and civilians for use in particular circumstances and threat scenarios. Currently, the US military uses a CB protective ensemble known as the Joint Service Lightweight Integrated Suit Technology (JSLIST) overgarment.[6] The JSLIST, when worn with gloves and boots as shown in Fig. 13.1, provides protection against CWAs for 24 hours. It is

13.1 Joint Service Lightweight Integrated Suit Technology (JSLIST).

designed for extended use, can be laundered every seven days, and is disposable after 45 days of wear, even if not contaminated. It contains a clean and breathable sorptive liner material as part of its textile structure. The JSLIST overgarment has an integral hood and raglan sleeve design which allows more freedom of movement. Its integrated suspenders (braces) allow individualized fitting for individuals of diverse sizes. Its wrap-around hook and loop leg closures allow ease of donning and doffing. Similar carbon-based, air permeable overgarments are used by many other countries.

Another US military clothing system is the chemical protective undergarment (CPU).[7] The CPU is a two-piece, snug-fitting undergarment worn under any standard duty uniform. It is a stretchable fabric that is designed to provide up to twelve hours of vapor protection, and it has a 15-day service life. The CPU is shown in Fig. 13.2. Civilian variants of these garments are also available.

13.2 Chemical protective undergarment (CPU).

Recent R&D efforts in individual CB protection have been on the development of advanced CB protective clothing systems that are lighter in weight with reduced thermal burden. The aim is to enable the future soldier to operate longer in a CB contaminated environment comfortably, safely, and effectively. One of the current emphases is on the use of selectively permeable membranes (SPMs) as a component in future soldier systems. SPM-based CB protective clothing systems are about a third to half the weight of the standard CB clothing systems, depending on the clothing system's specific materials and design. The development of such systems has demonstrated that it is possible to limit or eliminate the need for activated carbon, the use of chemical protective overgarments, the use of chemical protective undergarments, the use of rubber gloves, and the use of overboots. The elimination of any or all of these clothing items would represent significant weight, logistics concern, and cost reductions, as well as an increase in comfort. In addition to membranes in the form of films, electrospun nanofiber membranes and fabrics are being extensively investigated for applications in CB clothing.

Soldiers as well as civilians use special-purpose clothing such as the Improved Toxicological Agent Protective (ITAP) ensemble and the Self Contained, Toxic Environment Protective Outfit (STEPO) during emergency operations for chemical spills, toxic chemical maintenance, and clean-ups in environments with higher threat concentrations. The ITAP and STEPO are shown in Figs 13.3 and 13.4, respectively. The ITAP is used in Immediately Dangerous to Life or Health (IDLH) toxic chemical environments for up to one hour. It is used in emergency and incident response,

13.3 Improved Toxicological Agent Protective (ITAP) suit.

13.4 Self-contained Toxic Environment Protective Outfit (STEPO).

routine chemical activity, and initial entry monitoring. ITAP is a suit that offers splash and vapor protection, and dissipates static electricity. It can be decontaminated for reuse after five vapor exposures, and it has a 5-year minimum shelf life. US Air Force firefighters use the ITAP with a self-contained breathing apparatus (SCBA), a personal ice cooling system (PICS), and standard TAP gloves and boots.

The STEPO is a totally encapsulating protective ensemble that provides four hours of protection against all known CB agents, missile/rocket fuels, petroleum oil and lubricants (POL), and industrial chemicals. Explosive ordinance disposal (EOD) and chemical facility (depot) munitions personnel engaged in special operations in IDLH environments use the STEPO. It can be decontaminated for reuse after five vapor exposures. Since complete encapsulation is very cumbersome, the work duration in the suit is

strictly limited because of the limited air supply, and microclimate cooling is necessary for comfort. The STEPO has four hours of self-contained breathing and cooling capabilities. It has a tether/emergency breathing apparatus option. It also has a built-in, hands-free communications system. If the major concern is liquid splash protection, then full encapsulation may not be necessary. The use of a coverall or apron may be more appropriate. Such items are typically fabricated from the same type of materials that are used in fully encapsulating suits. Vapor protection is then sacrificed for increased comfort and mobility. The STEPO is shown in Fig. 13.4.

Another item is the Suit – Contamination Avoidance and Liquid Protection (SCALP). The SCALP is made of polyethylene-coated Tyvek^{R}, and it is worn over the standard overgarment. It is designed to protect the user and their overgarment from gross liquid contamination during short-term operations for up to one hour. Decontamination personnel also use it. The SCALP is shown in Fig. 13.5.

Similar special purpose clothing is available commercially. As with combat clothing, the special purpose clothing has limited wear time. It can be repeatedly cleaned and re-used, and repaired if not contaminated. These suits have different designs and protective capabilities; thus potential users must understand their capabilities in order to use them properly in different operational environments for specific durations of use.

13.3 Materials for chemical and biological (CB) protective clothing

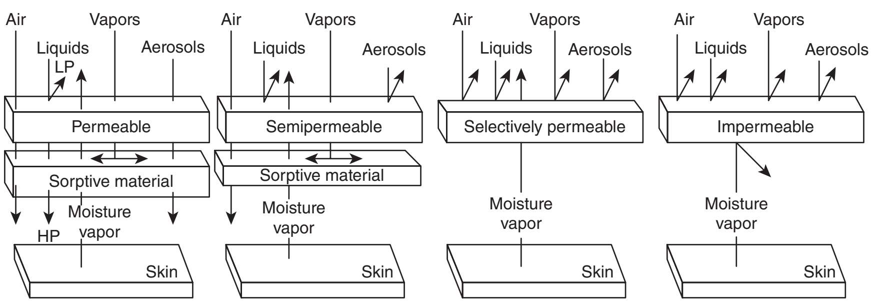
There are basically four different types of CB protective materials. These are illustrated in Fig. 13.6.

13.3.1 Air-permeable materials

Permeable fabrics usually consist of a woven shell fabric, a layer of sorptive material such as activated carbon impregnated foam or a carbon-loaded nonwoven felt, and a liner fabric. Since the woven shell fabric is not only permeable to air, liquids, and aerosols, but also vapors, a sorptive material is required to adsorb toxic chemical vapors. Liquids can easily penetrate permeable materials at low hydrostatic pressures; therefore, functional finishes such as Quarpel® and other fluoro-polymer coatings are usually applied to the outer-shell fabric to provide liquid repellency. Additionally, a liquid and/or an aerosol-proof overgarment such as non-perforated Tyvek® protective clothing must be used, in addition to permeable clothing, in a contaminated environment to provide liquid and aerosol protection. Many users like to use permeable clothing because convective flow of air is possible through the clothing and open closures. This action allows

Published by Woodhead Publishing Limited, 2013

13.5 Suit – Contamination Avoidance and Liquid Protection (SCALP).



13.6 Types of CB protective materials. LP, low hydrostatic pressure; HP, high hydrostatic pressure.

evaporative cooling to occur. Examples of air-permeable protective clothing containing activated carbon include garments used by the US, British, and Canadian military, as well as that of many other countries.

13.3.2 Semipermeable materials

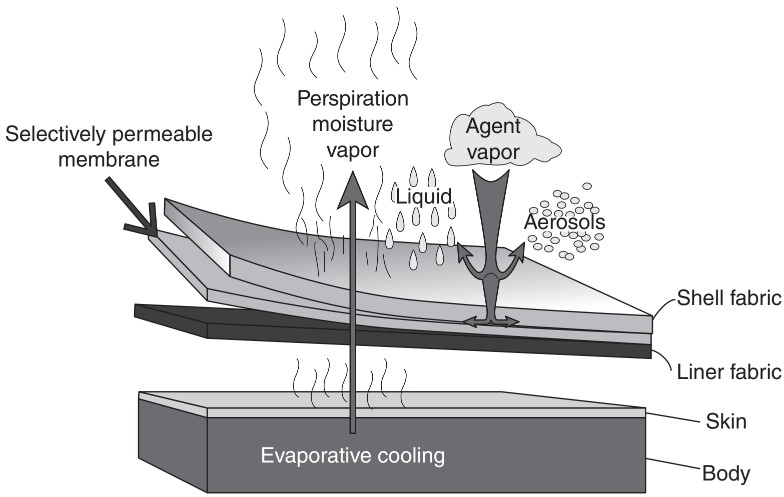
There are two different types of semipermeable membranes – porous and solution–diffusion membranes.[8] Porous membranes include macroporous, microporous, and ultraporous membrane structures. A macroporous membrane allows convective flow of air, aerosols, and vapors through its large pores. A microporous membrane follows Knudsen diffusion through pores, where pores with diameters less than the mean free path of the gas molecules allow lighter molecules to preferentially diffuse through. An ultraporous membrane has also been referred to as a molecular sieving membrane, where large molecules are excluded from the pores by virtue of their size. A solution–diffusion membrane has also been called a nonporous or a monolithic membrane. This type of membrane follows Fickian diffusion through the nonporous membrane, where gas dissolves into the membrane, diffuses across it, and desorbs on the other side based on concentration gradient, time, and membrane thickness. Such membranes have found many applications in sports clothing and related active wear.

13.3.3 Impermeable materials

Impermeable materials such as butyl and halogenated butyl rubber, neoprene, and other elastomers have been commonly used over the years to provide CB agent protection.[9] These types of materials, while providing excellent barriers to penetration of CB agents in liquid, vapor, and aerosol forms, impede the transmission of moisture vapor (sweat) from the body to the environment. Prolonged use of impermeable materials in protective clothing in the warm/hot climates of tropical areas, significantly increases the danger of heat stress. Likewise, hypothermia can readily occur if impermeable materials are used in the colder climates. Based on these limitations, a microclimate cooling/heating system can be an important adjunct to the impermeable protective clothing system, to compensate for its inability to allow moisture permeation.

13.3.4 Selectively permeable materials (SPMs)

SPMs are extremely thin, lightweight, and flexible protective barrier materials to CB agents and selected TICs, but without the requirement of a thick, heavy, and bulky sorptive material such as an activated carbon material layer. They allow selective permeation of moisture vapor from the body to



13.7 Selectively permeable membrane.

escape through the protective clothing layers so that the body of a soldier is continuously evaporatively cooled during his missions while being protected from the passage of hazardous chemicals in liquid, vapor, and aerosol forms. SPMs have the combined properties of impermeable and semipermeable materials. The protection mechanism of selectively permeable fabrics relies on a selective solution/diffusion process, whereas carbon-based fabrics rely on the adsorption process of activated carbon materials. SPMs have been widely used for many years throughout the chemical industry in gas separations, water purification, and in medical/metabolic waste filtration.[10] SPMs consist of multi-layer composite polymer systems produced using various different base polymers such as cellulose, cellulose acetate, polyallylamine, polyallylimine and polyvinyl alcohol, among other gas or liquid molecular separation membranes. SPMs are expected to see increasing applications in CB protection as future garments and items are developed. A schematic of an SPM is shown in Fig. 13.7.

13.4 Technologies for next generation chemical and biological (CB) clothing

13.4.1 Self-detoxification

Catalysts are under development that are intended to cause the transformation of chemical warfare agents (CWAs) into less hazardous chemicals. Some of this work is aimed at improving methods of detoxifying contaminated vehicles and equipment following a chemical attack. The chemistry behind traditional methods of decontamination has been reviewed by Yang

et al.[11] These agent-reactive catalysts can also be incorporated into fabric systems, where they serve to reduce the hazard from chemical contamination, particularly while doffing the contaminated clothing and disposing of it. The addition of catalysts to CB protective clothing systems is not a trivial matter. The catalysts can be applied as a coating onto fabrics or individual fibers; they can be incorporated within individual fibers; they can be chemically bonded to fiber surfaces; or they can be incorporated as particles or nanoparticles within a matrix such as an electro-spun nanofiber mat. Aspects of these approaches have been discussed by Sun *et al.*[12]

Numerous efforts to develop and incorporate catalysts are ongoing. Enzymes have been studied for this purpose for many years. Enzymes such as organophosphorus acid anhydrolase (OPAA) to neutralize G agents and VX have been developed. The widespread use of enzymes in these applications has been hindered by the lack of durability of the enzymes. The presence of water is also necessary for the successful hydrolysis of nerve agents. Work is ongoing to improve this property. This topic has been reviewed by DeFrank.[13]

Polyoxometallates (POMs) for neutralizing sulfur mustard (HD) have been studied extensively by Hill.[14] Recently, Song *et al.* reported that a POM has been incorporated into the pores of a metal-organic framework.[15] This novel catalyst has been found to dramatically increase the turnover rate of the POM in air-based oxidations.

One family of catalysts that has demonstrated effectiveness against a variety of hazardous chemicals are metal oxides, such as MgO, TiO_2, CaO, and Al_2O_3. The development and characterization of these catalysts have been reported by Wagner *et al.* In studies using solid-state MAS NMR, the nerve agents VX, GB, and GD, as well as HD, were reported to hydrolyze on the surface of metal oxide nanoparticles. In general, nontoxic by-products are formed.[16]

Bromberg *et al.* have studied the nucleophilic hydrolysis of organophosphorus compounds by polyacrylamidoxime (PANOx) and poly(N-hydroxyacrylamide) (PHA) and found these catalysts to be effective in degrading these chemicals.[17]

Halamines (R_2N-X, where X = Cl, Br, or I) are being investigated for use as biocides, as well as catalysts, in protective clothing.[18]

13.4.2 Super-repellency

When breathable clothing is contaminated by contact with droplets of hazardous chemicals, the droplets may 'wet' the fabric by soaking into it, or the droplets may remain on the surface and not wet the fabric. In either case, the vapors associated with the droplets will sooner or later permeate the fabric. To minimize the contact time between the droplets and the

protective garment, the outer shell fabric is usually treated with a liquid repellent coating such as Quarpel^{R}. While these finishes do a good job repelling liquid water and certain other chemicals, they may not be effective in repelling a variety of hazardous chemicals. Work is underway to develop fabric treatments that are super-repellent; that is, superhydrophobic and superoleophobic.

Aspects of the fundamental science behind super-repellency in fabrics have been developed by Tuteja *et al.*[19] and Chhartre, *et al.*[20] The fabrication of such fabrics for applications in CB protective clothing has been discussed by Saraf *et al.*[21] The idea is to develop fabric treatments that are sufficiently liquid repellent to allow droplets of chemicals to be easily shed from protective clothing. Such clothing can also be described as self-cleaning, since dirt and oils will not adhere to the clothing.

13.4.3 Electronic textiles

The integration of electronics into textile systems has made it possible to incorporate sophisticated functions into clothing that were not previously possible. The development of wireless technology has added a new dimension to these advancements. Some of the new functions now possible include physiological status monitoring, resistive heating, wearable power, and the incorporation of CB sensors. Wearable electronic systems have been described by Park and Jayaraman.[22]

For individuals such as soldiers and firefighters to perform their missions optimally, they must be in good physical condition. It is now possible for commanders and medics to wirelessly monitor the status of their physiological condition using sensors that are integrated into their clothing systems. Sensors are currently available that can monitor skin temperature, heart rate, respiration rate, and hydration status. Such monitoring can lead to improved readiness in medical treatment and in the treating of casualties.

Numerous technologies have been developed and incorporated into a range of CB detectors for use in buildings, at transportation hubs, and on the battlefield. Many of these technologies can be miniaturized and incorporated as small sensors into clothing systems, either on or within the textile structure. These technologies typically detect the presence of organophosphorus compounds or other hazardous chemicals.

13.4.4 Thermal management

For operation in extreme climates, it may be desirable to integrate some form of active or passive heating or cooling into clothing systems. Increased warmth can be achieved through the use of layers and insulation materials.

Active heating, using traditional wires or conductive fibers incorporated into the textile system, can also be used. Heated handwear is especially useful and welcome in cold climates.

Cooling can be achieved on a short-term basis through the use of phase-change materials. These materials have been incorporated into boots, helmets, and backpack liners and typically provide around an hour of cooling. Cooling vests have been developed that are able to provide effective cooling indefinitely. These vests utilize tubing which is sandwiched between two fabrics and through which cold water circulates. The water is cooled by a vapor compression cooling unit that is operated on battery power or power supplied by a vehicle. Vapor compression units powered by portable batteries add weight to already overburdened users, so their use by dismounted individuals remains strictly limited.

13.5 References

1. McWilliams, J. L. and R. J., *Steel, Gas! The Battle for Ypres, 1915*, Vanwell Publishing Limited: Deyell Co., Canada (1985).
2. Chemical Weapons – *Threat, Effects, and Protection*, FOI Swedish Defence Research Agency Briefing Book ON (2), p. 5 (2002).
3. Chemical Weapons – *Threat, Effects, and Protection*, FOI Swedish Defence Research Agency Briefing Book ON, p. 7 (2002).
4. Tu, A. T., *Chemical Terrorism: Horrors in Tokyo Subway and Matsumoto City*, Alaken, Inc., Fort Collins, CO (2002).
5. Carus, W. S., *The Illicit Use of Biological Agents Since 1900*, Working Paper – Bioterrorism and Biocrimes, National Defense University Center for Counterterrorism, Washington, DC (August 1998, February 2001 Revision).
6. Military Specification MIL-DTL-32102, JSLIST *Coat and Trouser*, *Chemical Protective*, 3 April 2002.
7. Military Specification MIL-U-44435, *Undershirt and Drawers, Chemical Protective and Flame Resistant*, 16 April 1992.
8. Ho, W. S. and K. K. Sircar, Eds., *Membrane Handbook*, Chapter 1, Van Nostrand Reinhold, New York, 1992.
9. Wilusz, E., in *Polymeric Materials Encyclopedia*, J. C. Salamone, Ed., p. 899, CRC Press, Boca Raton (1996).
10. Koros, W. and G. Fleming, *J. Membrane Sci.*, 83 (1993).
11. Yang, Y. C., J. A. Baker, and J. R. Ward, *Chem. Rev.*, 92, 1729–1743 (1992).
12. Sun, G., S. D. Worley, and M. Broughton, Self-decontaminating materials for protective clothing, Chap. 12 in *Military Textiles*, E. Wilusz, Ed., Woodhead Publishing Ltd, Cambridge, UK (2008).
13. DeFrank, J. J., Organophosphorus Cholinesterase Inhibitors: Detoxification by Microbial Enzymes, in *Applications of Enzyme Biochemistry*, J. W. Kelly, and T. O. Baldwin, Eds., Plenum Press, NY (1991).
14. Hill, C., *Chem. Rev.*, 98(1) (1998).
15. Song, J., Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle, and C. L. Hill, *J. Am. Chem. Soc.*, 133(42) 16839–16846 (2011).

16. Wagner, G. W., O. B. Koper, E. Lucas, S. Decker, and K. Klabunde, *J. Phys. Chem. B*, 104, 5118 (2000).
17. Bromberg, L., H. Schreuder-Gibson, W. R. Creasy, D. J. McGarvey, R. A. Fry, and T. A. Hatton, *Ind. Eng. Chem. Res.*, 48(3), 1650–1659 (2009).
18. Liang, J., J. R. Owens, T. S. Huang, and S. D. Worley, *J. Appl. Polym. Sci.*, 101(5), 3448–3454 (2006).
19. Tuteja, A., W. Choi, M. Ma, J. M. Mabry, S. A. Mazzelle, G. C. Rutledge, G. H. McKinley, and R. E. Cohen, *Science*, 318(5856), 1618–1622 (2007).
20. Chhartre, S. S., W. Choi, A. Tuteja, K. C. Park, J. M. Mabry, G. H. McKinley, and R. E. Cohen, *Langmuir*, 26(6), 4027–4035 (2010).
21. Saraf, R., H. J. Lee, S. Michielsen, J. Owens, C. Willis, C. Stone, and E. Wilusz, *J. Materials Sci.*, 46(17), 5751–5760 (2011)
22. Park, S. and S. Jayaraman, *MRS Bulletin* 28(8), 585–590 (2003).

Index